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THE FIFTH ANNUAL CONFERENCE  
ON HAN-BASED LIQUID PROPELLANTS

JOSEPHINE Q. WOJCIECHOWSKI  
EDITOR

JUNE 1990

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## INTRODUCTION

The US Army is currently investigating the use of liquid propellants (LPs) in large and medium caliber guns. These LPs are characterized by the use of hydroxylammonium nitrate (HAN) as their oxidizer. On 22-23 August 1989, the Fifth Annual LP Conference on HAN-Based Liquid Propellant Structure and Properties was held at the BRL with Mr. Charlie Leveritt as General Chairman. The papers presented at this highly successful conference were given by people from academia, industry, and other government agencies.

This report is a compilation of the abstracts and viewgraphs of these papers where available. The final program is included in appendix A and a list of attendees in appendix B.

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<b>Title of Paper</b>	The Effect of Pressure and Dissolved Gases on the Electrical Conductivity of Concentrated HAN solutions and Liquid Propellants					
<b>Presentation Time Request</b>	30	(min)				
<b>Type of Paper:</b>	X	<b>Progress;</b>	<b>Summary;</b>	X	<b>State-of-art;</b>	<b>Other</b>
<b>Speaker's Name</b>	S. Murad		<b>Phone Number</b>		(312) 996-5593	
<b>Affiliation/address</b>	Chemical Engineering University of Illinois at Chicago Chicago, IL 60680					
<b>Co-author(s) name(s)</b>	P. Ravi					

A generalized correlation based on extended corresponding states has been developed for the specific electrical conductivity of concentrated aqueous electrolyte solutions. The correlation can account for the effect of concentration, temperature, and pressure, with two adjustable parameters, which are state independent, but may be linearly dependent on concentration. The generalized correlation has then been tested for LGP 1845, LGP 1846, and 11M HAN solutions, to demonstrate its accuracy at atmospheric pressures. It has also been used to predict the effect of pressure, and dissolved gases on electrical conductivity. Although experimental data on liquid propellants or HAN solutions is not available at high pressures, tests with other systems for which such data are available show satisfactory agreement.

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THE EFFECT OF PRESSURE AND DISSOLVED GASES ON THE  
ELECTRICAL CONDUCTIVITY OF CONCENTRATED HAN  
SOLUTIONS AND LIQUID PROPELLANTS

S. Murad and P. Ravi  
University of Illinois  
Chicago

AUGUST 1989

## OUTLINE

A. SOLUBILITY OF GASES IN LIQUID  
PROPELLANTS

B. EFFECT OF DISSOLVED GASES ON  
PHYSICAL PROPERTIES

(i) DENSITY

(ii) ELECTRICAL CONDUCTIVITY

C. FUTURE WORK

## SOLUBILITY OF GASES IN LIQUID PROPELLANTS

GENERALIZED CORRELATION FOR SOLUBILITY,

$$x_i = \frac{f_i^{(G)}}{H_{i,s}^o \exp(P \bar{V}_i^\infty / RT)} \quad (1)$$

IN EQN.(1), THE UNKNOWN VARIABLES ARE

$$H_{i,s}^o, \bar{V}_i^\infty, \text{ AND } f_i^{(G)}$$

THESE CAN BE OBTAINED AS FOLLOWS:

$$\frac{f_i^{(G)}}{\quad}$$

PURE GASES

$$\ln\left[\frac{\bar{f}_i^{(G)}}{P}\right] = \int_0^P (Z_i - 1) \frac{dP}{P} \quad (2A)$$

OR FROM CHARTS IN STANDARD REFERENCES (E.G. PITZER/BREWER)

MIXTURES

$$f_i(G) = y_i f_i^{\text{pure}} \quad (2B)$$

$$\underline{\bar{V}_i^\infty}$$

$$V_i^* = -0.0156 + 33.258 T^*, \quad (3)$$

$$\text{WHERE} \quad V_i^* = \bar{V}_i^\infty P_i^c / RT_i^c \quad (3A)$$

$$\text{AND} \quad T^* = TP_i^c / C_S T_i^c \quad (3B)$$

$$\underline{H_{i,S}^*}$$

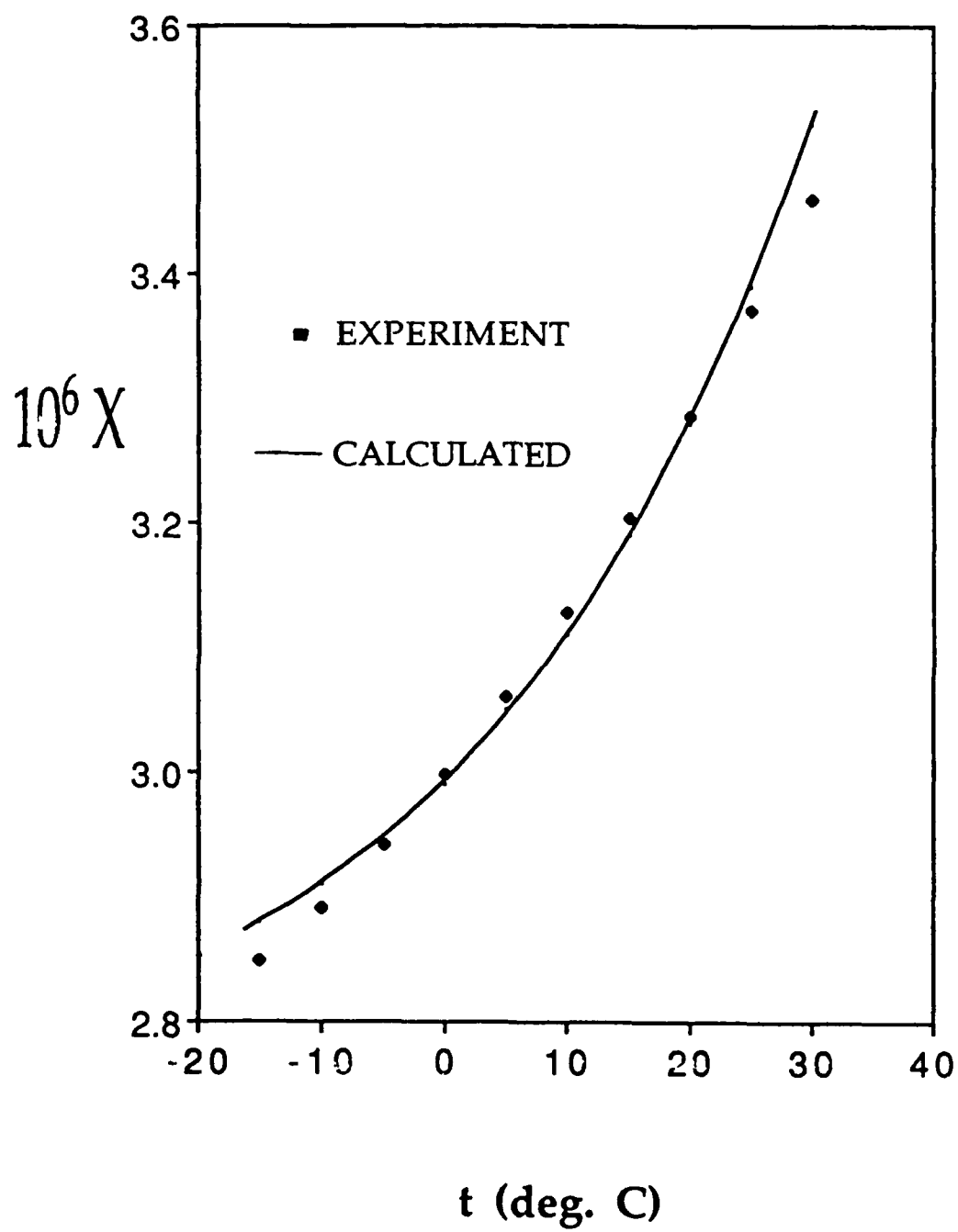
$$H_{i,S}^* = -206.7 + 3.992 T^* - 0.0126 T^{*2} \quad (4)$$

$$\text{WHERE} \quad H_{i,S}^* = H_{i,S}^0 / \beta_i \quad (4A)$$

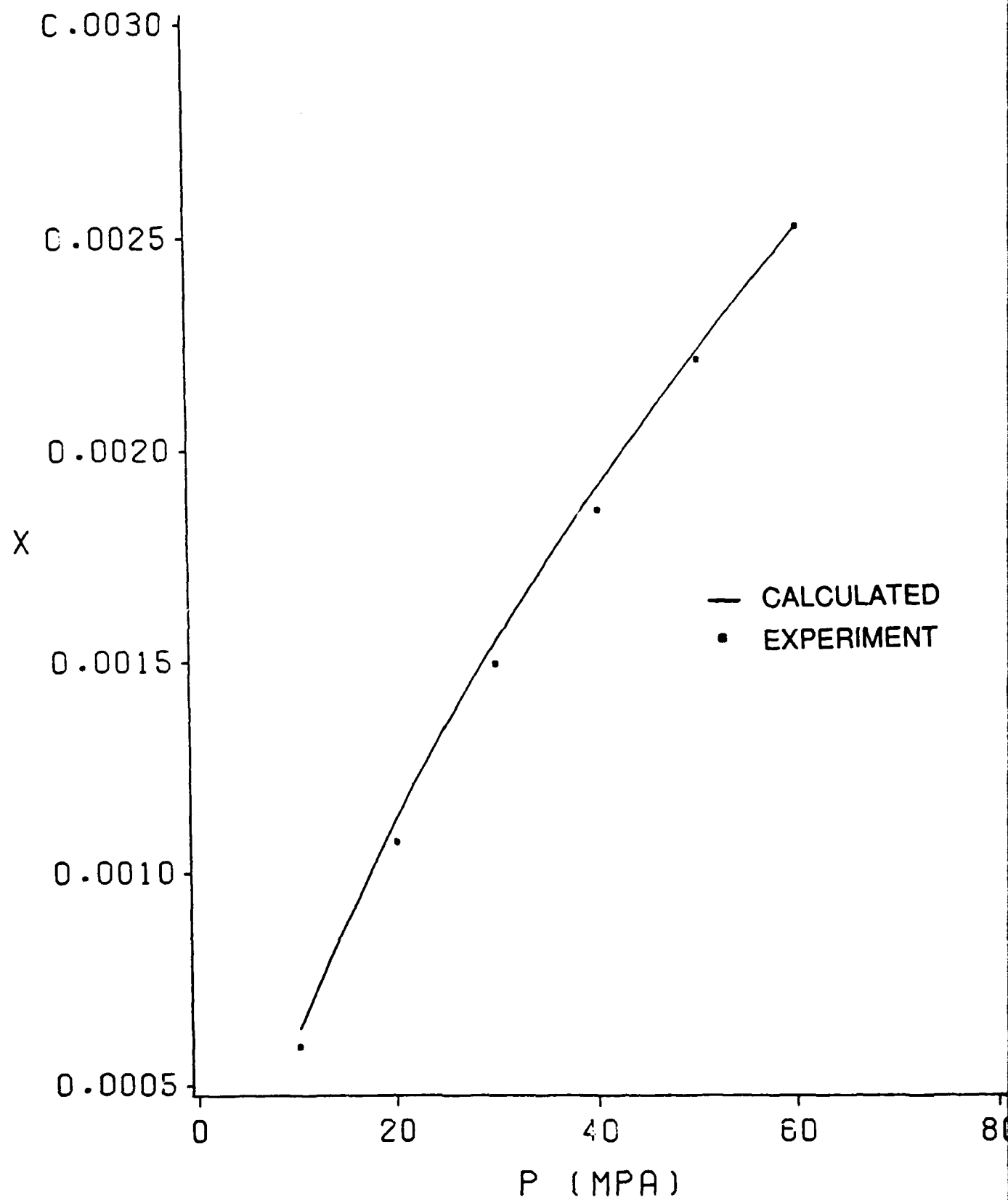
$$\text{AND} \quad T^* = T / \alpha_i \quad (4B)$$

WHERE  $\alpha_i$  AND  $\beta_i$  ARE COMPONENT PARAMETERS AND DEPEND UPON  $(P_i^c, T_i^c, MW)$ .

## SOLUBILITY OF NITROGEN IN LGP 1846



# SOLUBILITY OF N<sub>2</sub> IN 1m NaCl AT 51.5 °C

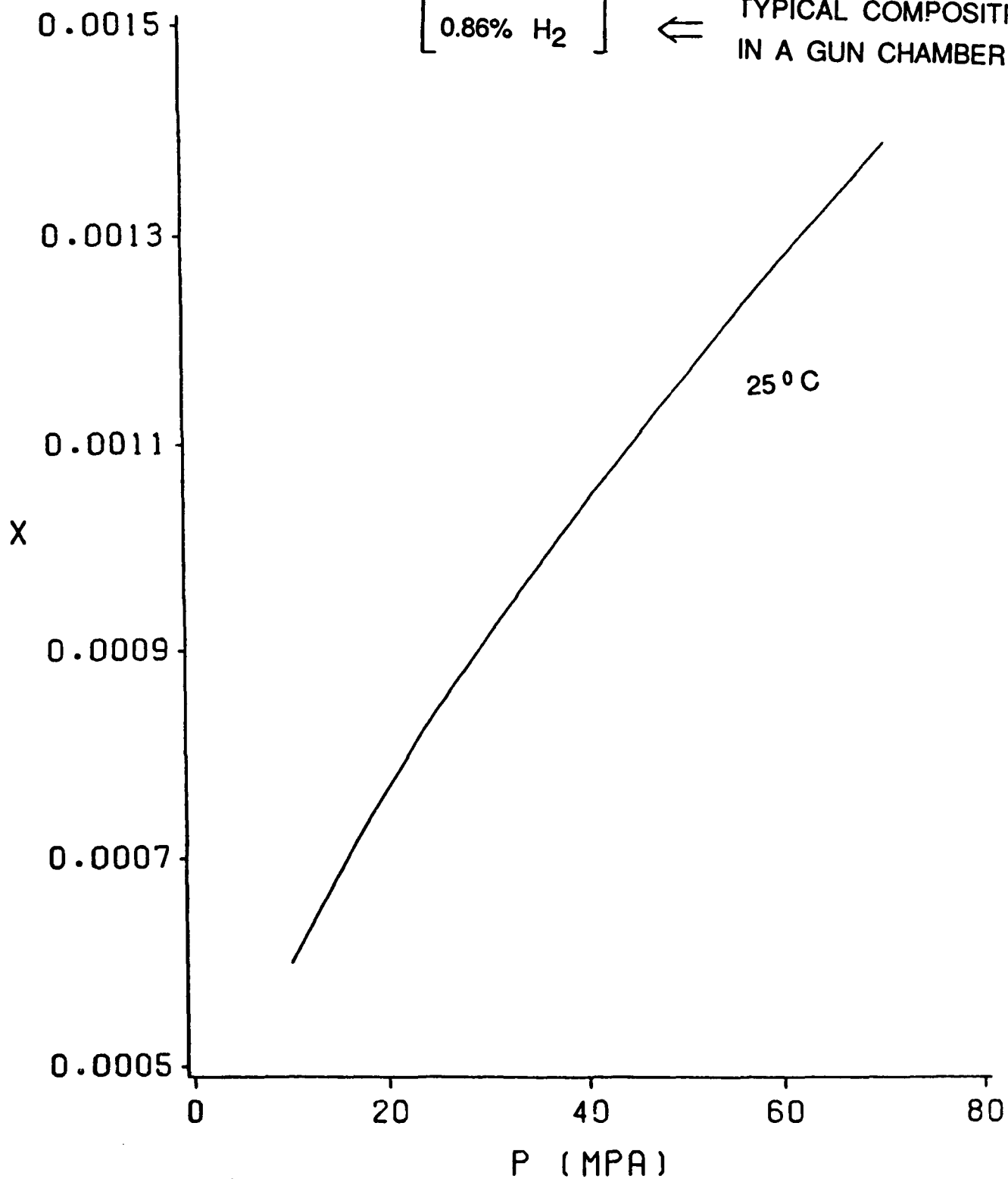


Solubility of

$\left[ \begin{array}{l} 56.59\% \text{ N}_2 \\ 41.52\% \text{ CO}_2 \\ 1.02\% \text{ CO} \\ 0.86\% \text{ H}_2 \end{array} \right]$

in LGP 1846

← TYPICAL COMPOSITION  
IN A GUN CHAMBER





## EFFECT OF DISSOLVED GASES ON DENSITY

THE DENSITY ( $\rho$ ) OF LGP 1845 AND 1846 CAN BE OBTAINED FROM THE EQUATION OF STATE DEVELOPED PREVIOUSLY.

TO ACCOUNT FOR THE EFFECT OF SOLUBILITY, THE DENSITY IS MODIFIED AS FOLLOWS:

$$\rho' \text{ (mol/cm}^3\text{)} = \frac{1.0}{\sum_i x_i \bar{V}_i^\infty + \frac{(1 - \sum_i x_i)}{\rho}} \quad (5)$$

WHERE  $x_i$  IS THE MOLE FRACTION AND  $\bar{V}_i^\infty$  IS THE PARTIAL MOLAR VOLUME OF GAS  $i$  IN THE LIQUID PROPELLANT

## ELECTRICAL CONDUCTIVITY

### STRATEGY

- (i) DEVELOP GENERALIZED CORRELATION FOR (T, X)
  - EXPERIMENTAL DATA AVAILABLE FOR LGP'S AND AQUEOUS SOLUTIONS USED
- (ii) ACCOUNT FOR EFFECT OF PRESSURE
  - EXPERIMENTAL DATA FOR AQUEOUS SOLUTIONS USED
- (iii) ACCOUNT FOR EFFECT OF DISSOLVED GASES
  - EXPERIMENTAL DATA FOR AQUEOUS SOLUTIONS AND MOLTEN SALTS USED.

## GENERALIZED CORRELATION FOR SPECIFIC CONDUCTIVITY

WE HAVE USED AVAILABLE EXPERIMENTAL DATA ON LGP 1845, 1846, HAN AND OTHER AQUEOUS ELECTROLYTE SOLUTIONS TO OBTAIN THE FOLLOWING EQUATION.

$$k^* = \frac{254.40}{T^{*1/2}} \exp \left( \frac{-348.75}{T^* - 142.24 - 0.00292 P^*} \right)$$

WHERE  $k^* = k (M \beta)^{1/2} \alpha^2$ , [k, S/cm]

$$T^* = T / \beta \quad [T, K]$$

$$P^* = P \alpha^3 / \beta \quad [P, \text{MPa}]$$

$\alpha$  AND  $\beta$  ARE EMPIRICAL PARAMETERS.

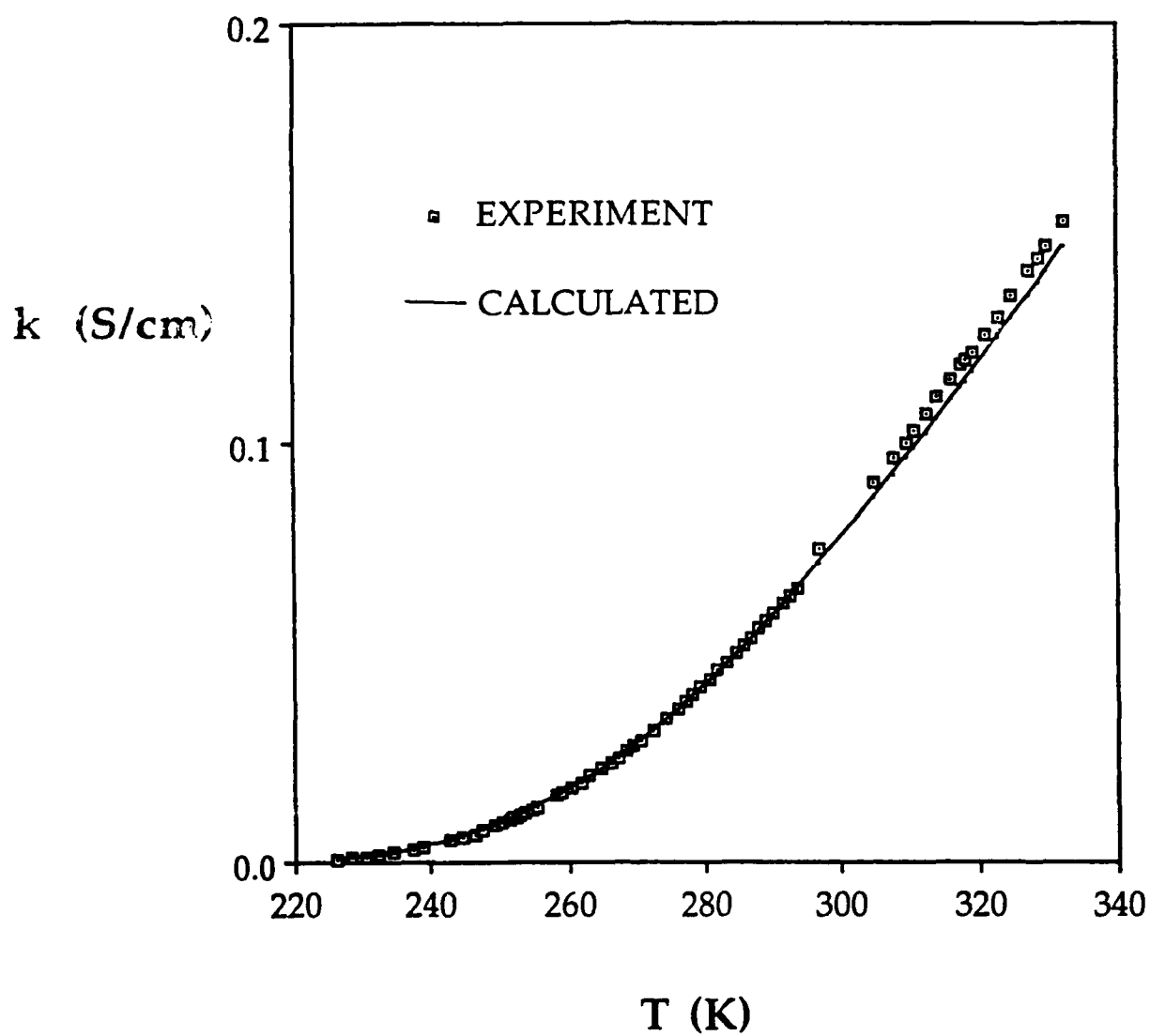
FOR HAN AND LGP'S THEY ARE GIVEN BY,

$$\beta = 1 + 0.50306 X \quad (\text{BOTH FOR HAN AND LGP'S}),$$

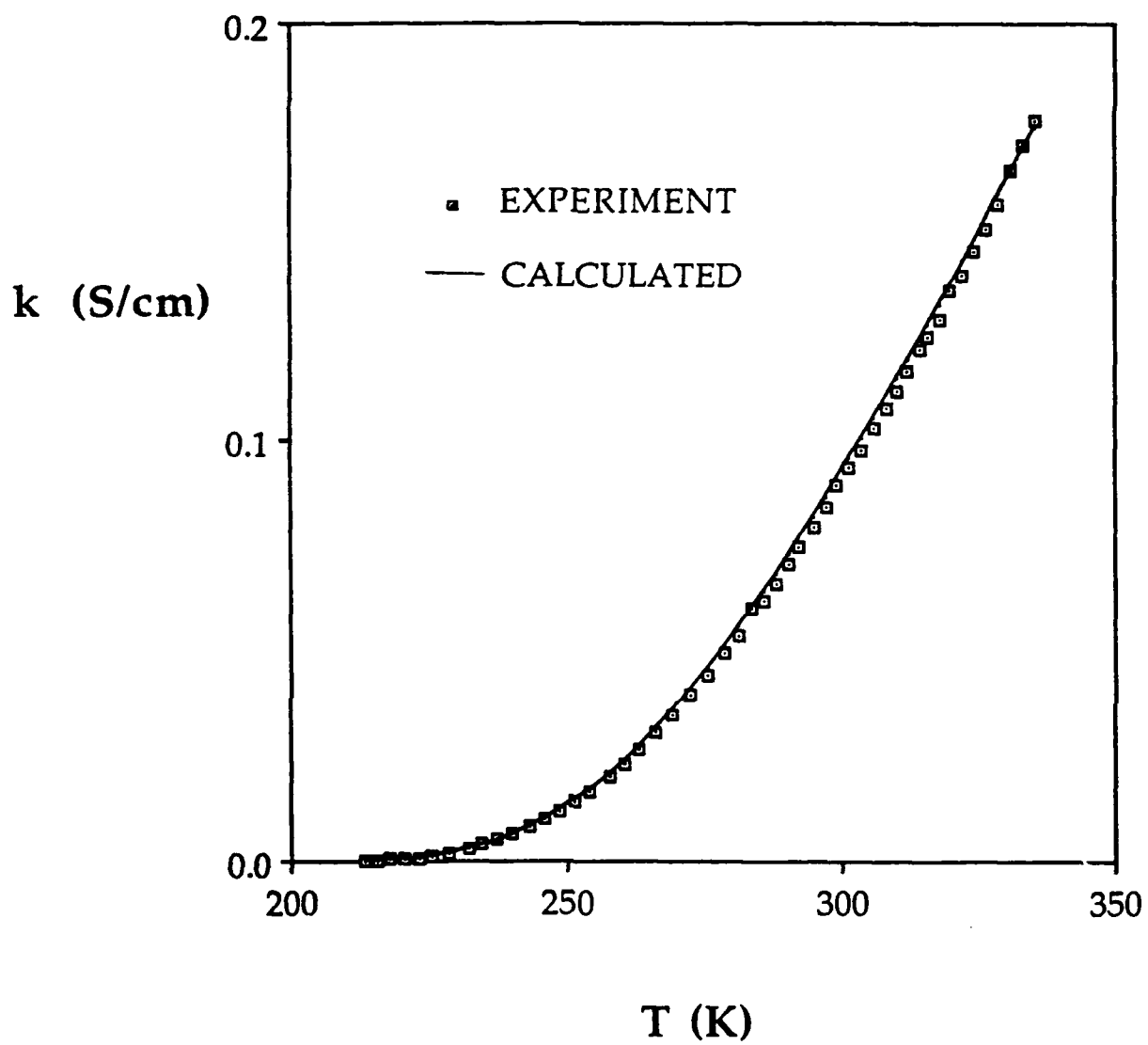
$$\text{LGP 1845, 1846: } \alpha = 1 - 0.1975 X$$

$$\text{HAN: } \alpha = 1 - 0.5328 X$$

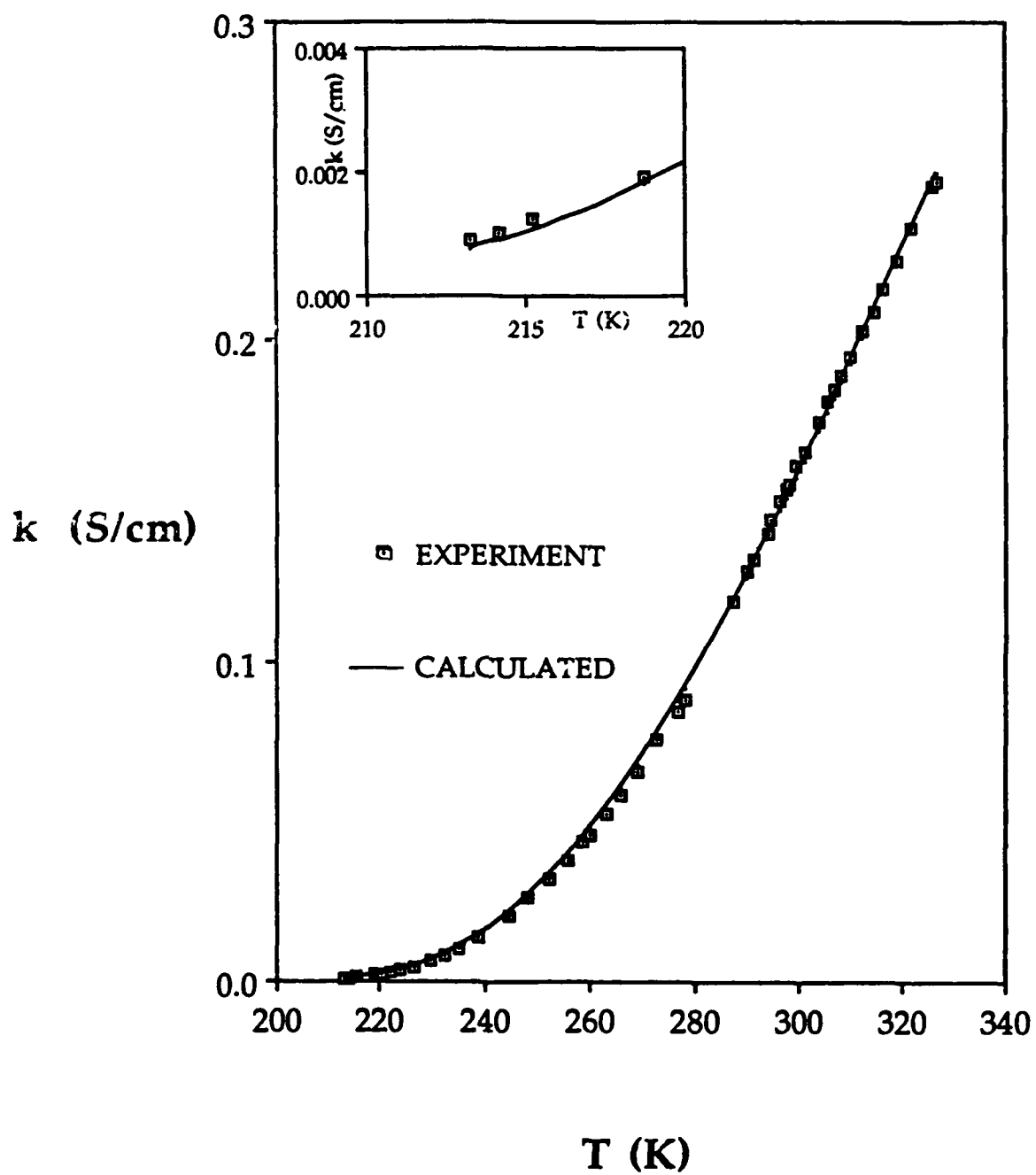
# SPECIFIC CONDUCTIVITY OF LGP 1845



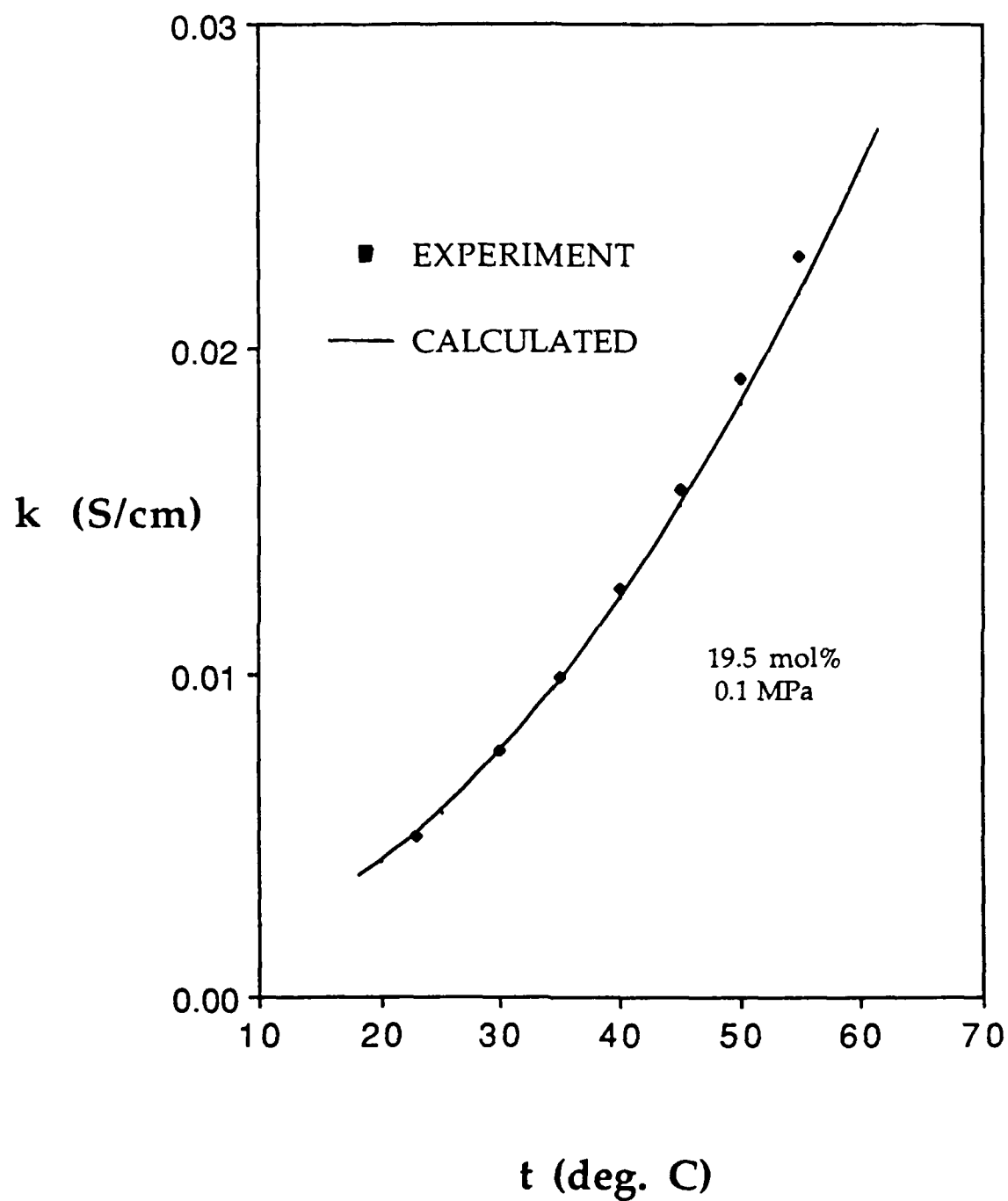
## SPECIFIC CONDUCTIVITY OF LGP 1846



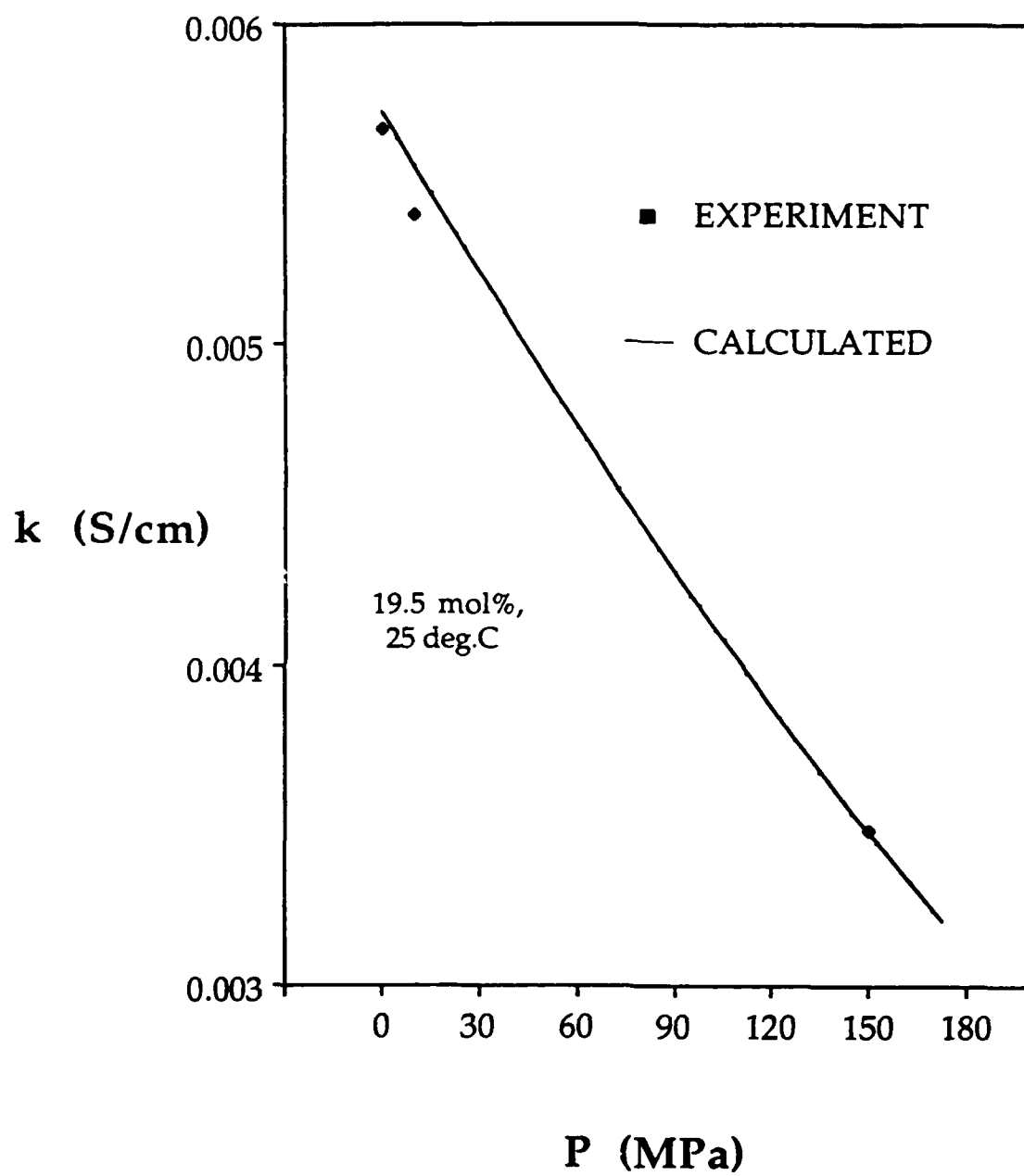
## SPECIFIC CONDUCTIVITY OF 11M HAN



# SPECIFIC CONDUCTIVITY OF $\text{Ca}(\text{NO}_3)_2$

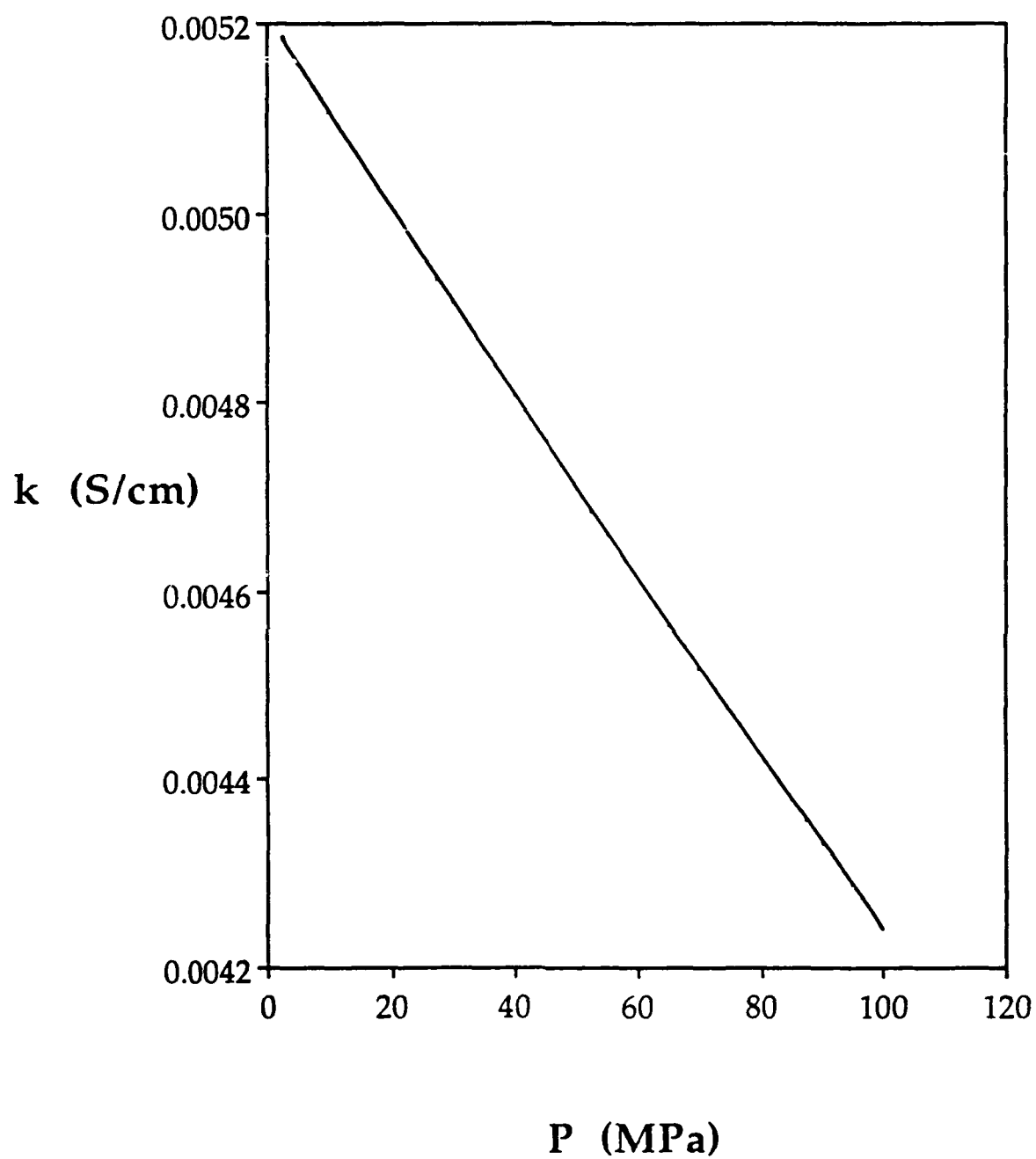


# SPECIFIC CONDUCTIVITY OF $\text{Ca}(\text{NO}_3)_2$

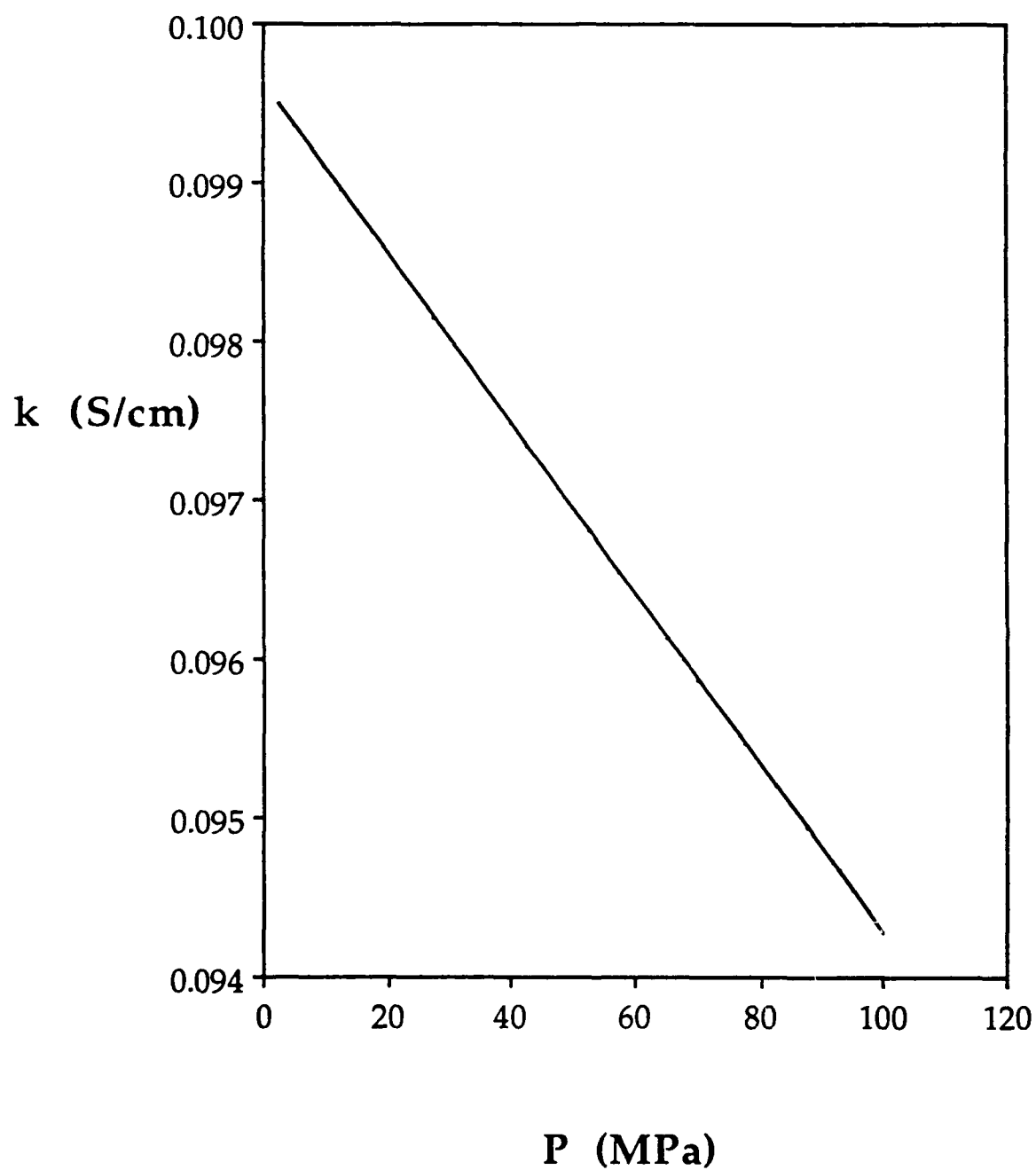




# SPECIFIC CONDUCTIVITY OF LGP 1845 AT -30 deg.C



# SPECIFIC CONDUCTIVITY OF LGP 1846 AT 30 deg.C



## EFFECT OF DISSOLVED GASES ON SPECIFIC CONDUCTIVITY

### KEY ASSUMPTION

THE EFFECT OF THE DISSOLVED GAS IS PRIMARILY ONE OF DILUTION (ION MOBILITY AND DISSOCIATION ARE ASSUMED UNCHANGED). THIS ASSUMPTION IS VALIDATED IF ONE EXAMINES THE SPECIFIC CONDUCTIVITIES OF DILUTE ELECTROLYTE SOLUTIONS.

THIS LEADS TO THE EQN,

$$\frac{k_2}{k_1} = 2.0165 - 1.2667 \left(\frac{V_2}{V_1}\right) + 0.24996 \left(\frac{V_2}{V_1}\right)^2,$$

WHERE  $\frac{V_2}{V_1}$  IS THE CHANGE IN VOLUME UPON DILUTION

AND  $\frac{k_2}{k_1}$  IS THE CHANGE IN CONDUCTIVITY.

THE CHANGE IN VOLUME UPON DISSOLUTION OF THE GAS  
CAN BE OBTAINED FROM,

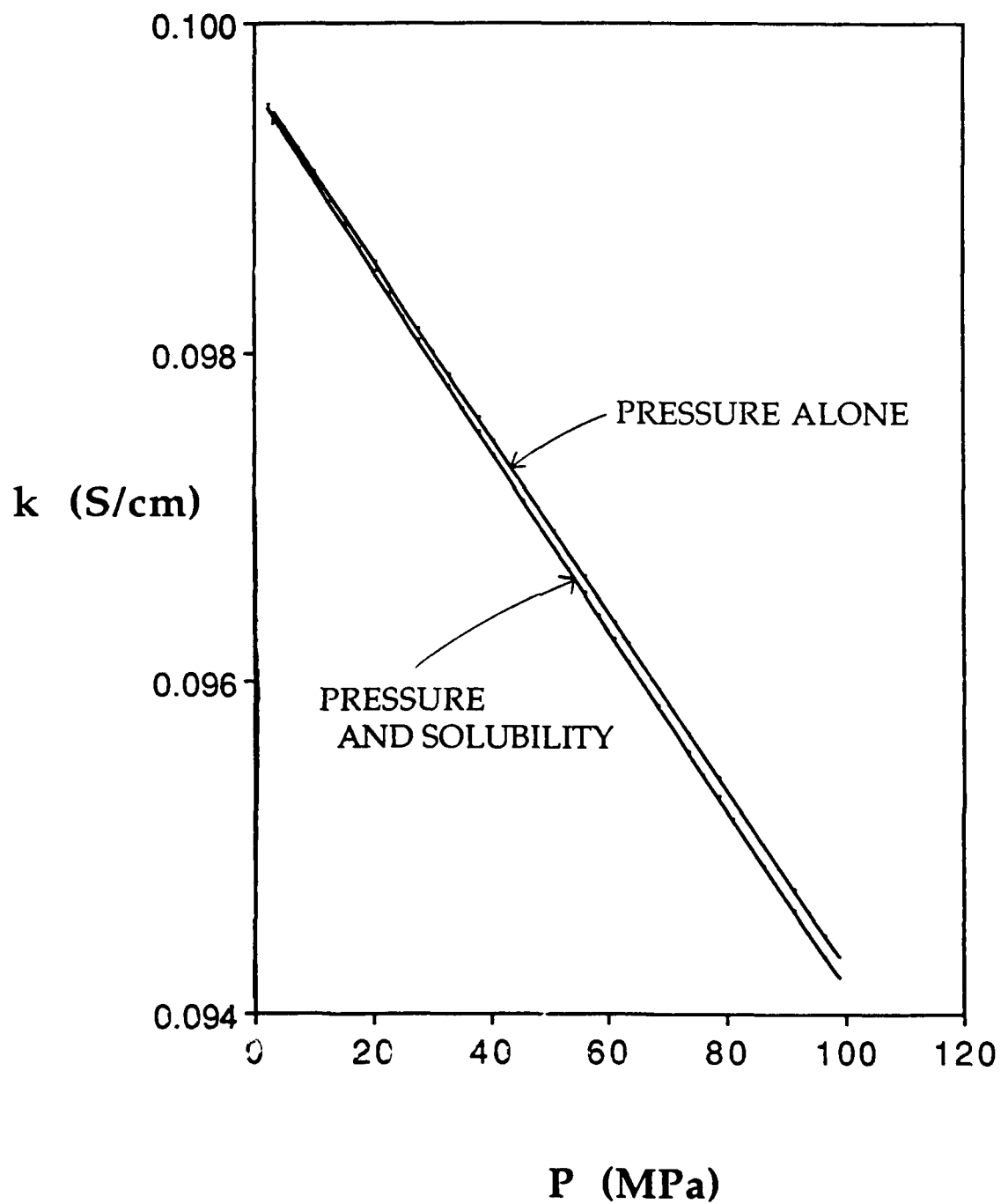
$$\frac{V_2}{V_1} = \frac{\sum_i X_i \bar{V}_i^\infty}{1 - \sum_i X_i} \rho' + 1.0,$$

WHERE  $x_i$  IS THE MOLE FRACTION OF THE GAS  $i$ ,

$\bar{V}_i^\infty$  IS THE PARTIAL MOLAR VOLUME OF THE GAS,

$\rho'$  IS THE CORRECTED DENSITY OF THE SOLUTION.

EFFECT OF SOLUBILITY OF N<sub>2</sub> ON THE SPECIFIC CONDUCTIVITY  
OF LGP 1846 AT 30 deg.C



## EXTENSION TO AN ARBITRARY PROPELLANT

### "LGP 184X"

EXAMPLE, ONE WITH COMPOSITION THAT IS IN BETWEEN  
1845 AND 1846.

	<u>HAN</u>	<u>TEAN</u>	<u>WATER</u>	
WT%	59.29	18.71	22.00	(LGP 184X)

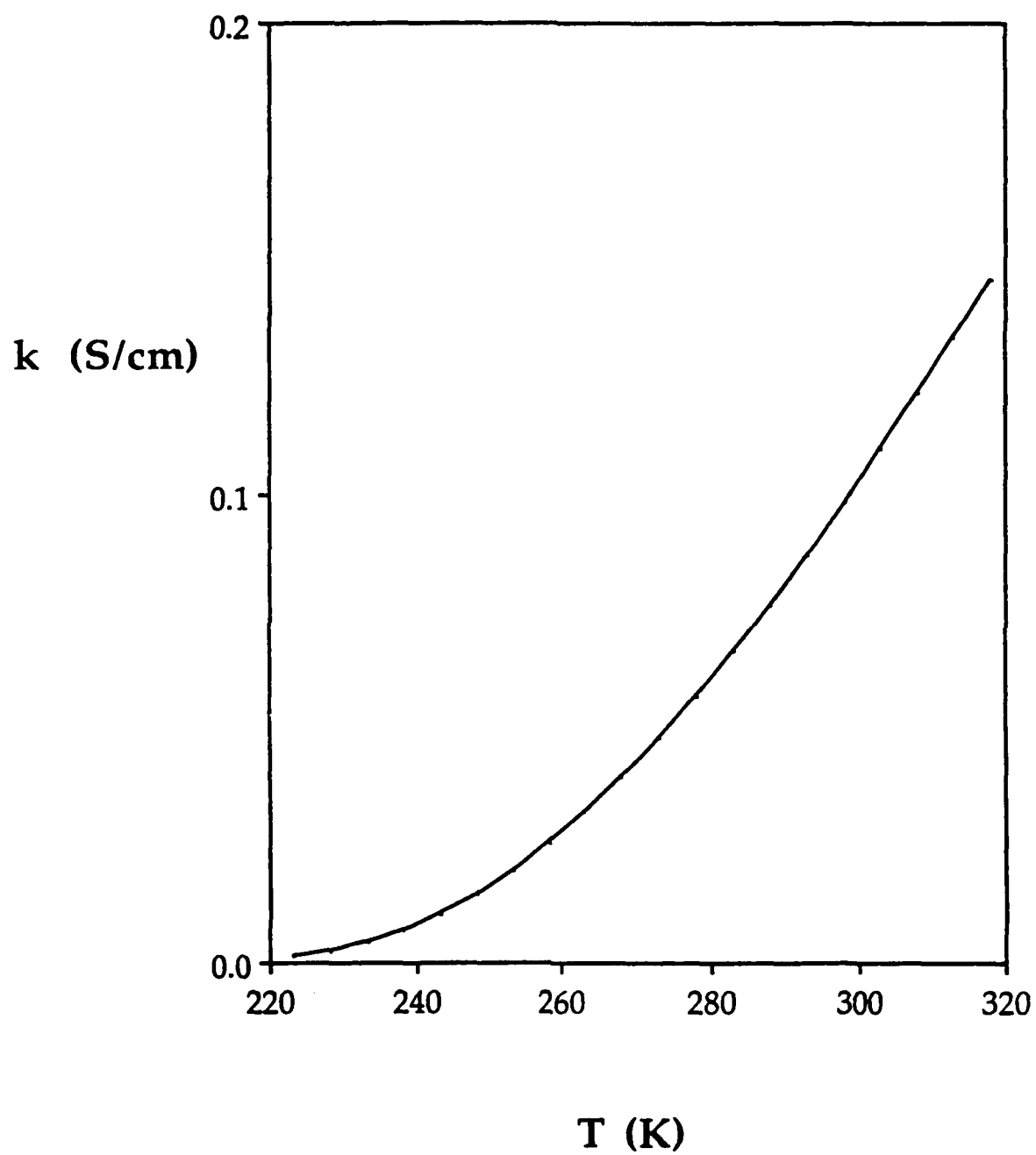
THEN

$$k^* = \frac{254.40}{T^{*1/2}} \exp \left( \frac{-348.75}{T^* - 142.24 - 0.00292 P^*} \right)$$

AND  $\alpha = 0.9277$

$$\beta = 1.1843$$

## SPECIFIC CONDUCTIVITY OF 184X



## SIMPLIFIED EQUATIONS FOR THE SPECIFIC CONDUCTIVITY OF LGP 1845 AND 1846

### PRESSURE EFFECT

$$\left(\frac{k_P}{k_1}\right) = \left(\frac{\rho_P}{\rho_1}\right)^2 \left(\frac{\eta_1}{\eta_P}\right)^{\delta^*}$$

$$\text{WHERE } \delta^* = 9.9226 - 0.0347 T^*$$

T\* REFERS TO THE VALUES AT ATMOSPHERIC PRESSURE AT THE SAME TEMPERATURE.

### TEMPERATURE EFFECT

$$\left(\frac{k_T}{k_{\text{ref}}}\right) = \left(\frac{\rho_T}{\rho_{\text{ref}}}\right)^2 \left(\frac{\eta_{\text{ref}}}{\eta_T}\right)^{\gamma^*}$$

$$\text{WHERE } \gamma^* = 1.4473 - 1.0978\text{E-}3 T^* - 1.0588\text{E-}3 T^{*\text{ref}}$$

THIS EQUATION CAN BE USED TO CALCULATE THE SPECIFIC CONDUCTIVITY AT ANY TEMPERATURE GIVEN THE VALUE AT ANY OTHER TEMPERATURE IN THE RANGE -45 TO +55 deg.C.



## FUTURE WORK

- A. THERMAL CONDUCTIVITY OF HAN, TEAN SOLUTIONS AND LIQUID PROPELLANTS, INCLUDING EFFECT OF DISSOLVED GASES
- B. EFFECT OF DISSOLVED GASES ON VISCOSITY (EFFECT OF T, P, X PREVIOUSLY INVESTIGATED)
- C. HEAT CAPACITY AS A FUNCTION OF (T, P, X) AND DISSOLVED GASES
- D. DIFFUSION COEFFICIENT

# ESTIMATING SOLUTION DENSITIES FOR MIXTURES CONTAINING HAN

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Olin Chemicals  
Charleston, Tennessee

## ABSTRACT

A correlation has been found that predicts apparent molar volume for HAN and other compounds of interest including ammonium nitrate, ammonium hydroxide, TEAN, and nitric acid. Apparent molar volume is correlated to a function of the combined mole fraction solute and thus enables estimation of the density of mixed solution. This correlation has been found to be more accurate than previous methods used to describe solutions of electrolytes and has a theoretical basis.

## INTRODUCTION

In the course of developing a detailed material and energy balance for the electrochemical production of HAN, we need to predict the density of mixed electrolytes, principally HAN, nitric acid, and ammonium nitrate. The density of a mixed salt cannot be accurately estimated based on existing correlation of density to the molarity of single components. Furthermore, when performing a mass balance, the molarity cannot be computed until the density is estimated.

W. M. Clarke of Olin Corporation has developed a method of predicting density for mixed concentrated electrolytes that fits a very wide range of inorganic compounds including sodium hydroxide and sodium chloride mixtures. This method has been found to work well even for slurries of mixed crystalline solids in their saturated mother liquor. Clarke's density correlation has been adopted for use in the ASPEN physical property database, but is still not widely known or used in industry.

This paper will discuss the application of Clarke's correlation to solutions containing HAN, including liquid propellant formulations. I will discuss the theoretical underpinnings of Clarke's formula and speculate on why it seems to work so well. I will also show the work I have done fitting data on ammonium nitrate solutions of different temperatures using Clarke's formula. This last work shows how electrolytes can affect the structure of water.

## EXPERIMENTAL DATA

Experimental data for this work was collected from a variety of existing sources. Reports from BRL were the source of data for my density correlations for HAN and TEAN. Data on ammonium nitrate and nitric acid were obtained from sources listed in the references.

## RESULTS AND DISCUSSION

### Theory and Equations:

The apparent molar volume is obtained by assuming that the volume of the solution can be divided into two portions, one contributed by the water and the other by the solute. The partial molar volume of the solute is determined by subtracting the volume of water, estimated from the density of pure water, from the density of the solution and subtracting the density of the solute. A useful formula for calculating the apparent molar volume from the density of pure solvent and molality of the solution is as follows:

$$1. \quad V' = \frac{1000}{m} \left( \frac{1}{\rho} - \frac{1}{\rho_0} \right) + \frac{M_2}{\rho_0}$$

For data available on the density of HAN and TEAN, concentrations were expressed in molarity rather than molality. The conversion from molarity to molality can be expressed as follows:

$$2. \quad m = \frac{1000M}{1000\rho - MM_2}$$

From the molality, the mole fraction solute can be calculated easily. Note that all solutes are considered to be single solution species even though they may dissociate into multiple ions.

$$3. \quad X = \frac{m}{m + 1000/M_1}$$

W. M. Clarke studied several methods for density correlation and found that Dave Thomas of Amoco used the Debye-Huckel equation for predicting activity coefficients with partial success as a correlation for the apparent molar volume. He tried a simplification of this equation, substituting mole fraction solute for ionic strength. Surprisingly, this simpler expression based on mole fraction of solute rather than molarity fits well for a wider range of solutions than the original Debye-Huckel expression. This expression is:

$$4. \quad \frac{\sqrt{X}}{1 + \sqrt{X}}$$

For solutions at infinite dilution, this expression goes to zero. Clarke's expression evaluates to 0.5 for anhydrous electrolyte.

To estimate density, existing density data is converted to apparent molar volume, and plotted as a function of Clarke's expression. A regression of the line is used to obtain coefficients from which the apparent molar volume at infinite dilution and for the pure electrolyte are extrapolated. Density for a given molality of solute can be estimated by first computing the mole fraction of solute as before, computing a predicted apparent molar volume, and then calculating density by an inversion of Formula 1.

$$5. \quad \rho = \frac{1000 + M_2 m}{V'_m + 1000/\rho_0}$$

For mixed electrolytes, the partial molar volume of each component is estimated separately, based on the combined total mole fraction solute. Formula 5 is modified to include the volume contributions of each species to the total.

$$6. \quad \rho_{\text{mix}} = \frac{1000 + (\sum M_2 m)}{(\sum V'_m) + 1000/\rho_0}$$

From the estimated density, we can calculate a conversion from molality to molarity for each component. This is useful in predicting the results of a volumetric analysis based on a density measurement. We have also used this conversion to compute molar compositions in our material balance.

The fit of Clarke's correlation to density data for HAN and TEAN is shown in Figures 1 and 2 and Table I. Both HAN and TEAN data fit this model extraordinarily well. Deviation from linearity is negligible even through points for 95% HAN. The extrapolation of the solution data to pure HAN gives a figure that is closer to the density of the HAN melt than for crystalline HAN. In Table I, the predicted densities are calculated from predicted molar volume and these agree with the original data very well, especially at low concentrations. The increasing accuracy of density predictions at low concentration is a significant benefit of our approach.

The slope of the line shows that at low concentrations, the apparent molar volume of HAN in water is lower than at high concentrations. This behavior is the same for most salts that fully dissociate in solution. In general, this behavior suggests that solvated ions in dilute solution become tightly wrapped in solvent and that the water in the vicinity of these ions forms a denser structure than free water.

Nitric acid is one compound that does not fit Clarke's correlation well (see Figure 3 and Table IV). The curve has a sharp bend at a mole fraction nitric acid of about 40%. This bend might be explained by the equilibrium of nitric acid with dissolved  $\text{N}_2\text{O}_5$  at high concentrations, or it could imply that nitric acid no longer dissociates at concentrations above 6M. This latter case seems more likely. For cases where the total acidity of solution is low, nitric acid can be assumed to have a nearly constant apparent molar volume of 30 cc/mole.

Ammonium hydroxide in Figure 5 and Table II (as ammonia) is one of the few compounds whose apparent molar volume is higher for dilute than concentrated solutions. This behavior may imply that in dilute solution, ammonia tends to insert itself into hydrogen bonded rings or chains, thus creating a more open structure.

Data for ammonium nitrate were available at a range of temperatures from 0 to 80 degrees Celsius. The curves for these data are shown in Figure 4 and Table II. The effect of temperature on the fit to Clarke's formula is particularly interesting at low temperatures. From 25 to 80 degrees Celsius, increasing temperature simply increases the apparent molar volume of the solute at about the same rate as that of water (0.05% per degree). However at 10 and 0 degrees Celsius, the plot AMV vs Clarke's expression is curved. At low concentrations, the slope of the curve is greater and the apparent molar volume appears to decrease rapidly at lower temperatures.

One explanation for this sharp deviation in the behavior of simple electrolytes at low temperatures is that the structure of water is changing and becoming more ordered and ice-like. This phenomenon is easily observed in the plot of specific volume of water as a function of temperature in Figure 6 and Table III. Ammonium nitrate ions act to decrease this rearrangement of water molecules and thus have

a greater densifying effect at low temperature than at high temperature. In essence, what we are saying is that the structure of water in a concentrated electrolyte at low temperature is similar to that of a more dilute electrolyte at higher temperature.

We have tested several other density correlations with much less success. For example, apparent specific volume of the solute correlates with the square-root of weight fraction solute. This correlation works well for HAN, but not at high concentrations, and not as well as Clarke's method. Other authors have shown correlations between apparent molar volume and various functions of molality, molarity, and mole fraction solute. All of these formulas have difficulty dealing with concentrated electrolytes accurately. Some rely on application of more than two coefficients.

Clarke's method has been applied to a variety of salts for which the correlation for dilute and concentrated solutions extrapolates accurately to the crystalline density of the salt. This is true for sodium chloride and sodium hydroxide (1:1); barium chloride (2:1), sodium sulfate (1:2) and cadmium sulfate (2:2). It also works for monobasic, dibasic, and tribasic sodium phosphate (1:3). Ferric chloride is an example of a 3:1 salt that also fits Clarke's model. Phosphoric, sulfuric and hydrochloric acid fit very well.

The simplicity of Clarke's method for density correlation is a very big advantage since it allows accurate prediction from a very small number of data points. In the absence of better information, this method may be used based on the crystalline density and the density of a single solution of known composition. Clarke's method is also the only one simple enough to allow the easy extraction of data about a desired compound from density measurements on a mixture of several electrolytes.

Why does Clarke's method work so well? We are not sure if there is a strong theoretical basis for this correlation since the form of this expression has no obvious physical significance. Clarke's method actually predicts the non-ideality of electrolytes since ideal solutions have a constant apparent molar volume for all mole fractions solute.

One interesting algebraic manipulation demonstrates that Clarke's expression can be rearranged to the form of the quadratic formula by transforming mole fraction solute to the solute/solvent mole ratio. This form of our expression suggests that the solute/solvent mole ratio is a simple parabolic function of the apparent molar volume. This makes sense if we see the solute/solvent ratio as providing a driving force for compression of some simple elastic bonds. Developing a more detailed theory along these lines might be a good opportunity for computerized molecular modeling.

I have used the coefficients for HAN and TEAN to estimate the density for LP-1845 and LP-1846 in Table III. This table is taken from a worksheet where the composition can be varied and the results are instantly updated. A similar set of formulas was used to estimate densities for solutions in the material balance for the electrochemical process for manufacturing 13 molar HAN.

Further use of the data on HAN will be for process control. Using this correlation, we can develop a cure to predict the concentration of HAN given the temperature and density. Completion of an accurate correlation with respect to temperature will require additional experimental data.

A copy of the worksheets from which all of the tables in this report were made is available from the author.

## CONCLUSION AND RECOMMENDATIONS

W. M. Clarke's correlation for densities of electrolytes has been shown to work remarkably well for HAN and TEAN solutions. This method provides a good basis for predicting the densities of LP formulations containing HAN, TEAN, and excess nitric acid. The fact that HAN and TEAN solutions fit this model so well suggests that they are indeed fully ionized, even in highly concentrated solutions.

Recent data on the density of LP formulation suggest that small changes in the excess nitric acid have a larger effect on density than that predicted by this method. We should consider whether small

Recent data on the density of LP formulation suggest that small changes in the excess nitric acid have a larger effect on density than that predicted by this method. We should consider whether small changes in excess nitric acid concentration could have the effect of converting a small equilibrium amount of free hydroxylamine to hydroxylammonium ions. As has been shown for ammonia and ammonium nitrate, a free amine can have the opposite effect on the structure of water from its corresponding ion.

Beyond the practical application of this method of density prediction, I believe that some useful theoretical implications can be drawn about the nature of water in LP formulations. I anticipate that as has been shown for ammonium nitrate and ammonia, the effect of temperature on the apparent molar volume of the solute reveals some useful hints about the interaction of water and electrolyte. If small amounts of free hydroxylamine can promote formation of hydrogen bonded chains, then reducing the free amine content by addition of slight excess nitric acid may improve the low temperature viscosity of LP.

In order to understand more about this phenomenon, I propose that density data be collected on HAN/water and TEAN/water solutions at low temperature, and for HAN solutions that have been over-neutralized (i.e., with free hydroxylamine). This information would be used to observe the relative effect of hydroxylammonium and triethanolammonium ions on the structure of water. An accurate estimate of the apparent molar volume of hydroxylamine will allow a test of my theory about low levels of nitric acid. Viscosity measurements will also help to evaluate my proposition.

Future work with other salts would allow the estimation of apparent molar volume of the individual ions. This information would help to create a more complete understanding of the structure of water in concentrated HAN.

## GLOSSARY

V'	Apparent molar volume	cc/mole
m	Molality	mole/100 gm solvent
$\rho$	Density of solution	gm/cc
$\rho_0$	Density of pure solvent	gm/cc
M <sub>1</sub>	Molecular weight of solvent	
M <sub>2</sub>	Molecular weight of solute	
M	Molarity of solution	mole/liter
X	Mole fraction solute	dimensionless

## ACKNOWLEDGEMENT

I would like to thank R. Sasse and W. M. Clarke for providing their great assistance to this work.

## LITERATURE CITED

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2. Perry and Chilton, Chemical Engineer's Handbook, pg 3-74 and 3-76, Fifth Edition, 1973.
3. Clarke, W. M. , "Densities of Aqueous Salt Solutions", unpublished.
4. Atkinson, Kumar, and Atkinson, "Modeling the PVT Properties of Concentrated Electrolytes in Water", University of Oklahoma, Departments of Chemistry and Physics, Norman, Oklahoma, unpublished.

Table I  
Density Correlation for HAN and TEAN

Original Data from SASSE et al Density of Hydroxylammonium Nitrate Solutions Memorandum Report BRL-MR-3720, December, 1988										
HAN	96.04	Molarity	Molality	Mole Fraction	A. Molar Volume	Clarke's Formula	Predict. M. Volume	Predict Density	Residual Error	Molar Volume vs Clarke's Formula Regression Output:
Density										
0.99963	0.000	0.000	0.000	0	48.500	0.0000	47.1141	0.9996	0.0000	Constant 47.114138
1.02341	0.500	0.513	0.0091425	0	50.857	0.0873	48.7917	1.0233	-0.0001	Std Err of Y Est 0.2190957
1.12533	2.781	3.240	0.0551049	50.857	52.178	0.1901	50.7687	1.1256	0.0003	R Squared 0.9932711
1.22919	5.232	7.198	0.1146957	52.178	52.785	0.2530	51.9772	1.2305	0.0013	No. of Observations 7
1.29636	6.858	10.749	0.1621199	52.785	53.529	0.2871	52.6322	1.2977	0.0014	Degrees of Freedom 5
1.37548	8.839	16.774	0.2319142	53.529	54.578	0.3250	53.3623	1.3775	0.0020	
1.52306	12.622	40.540	0.4218708	54.578	55.891	0.3938	54.6833	1.5210	-0.0020	X Coefficient(s) 19.222645
1.65569	16.338	187.272	0.7712141	55.891	57.168	0.4676	56.1021	1.6500	-0.0057	Std Err of Coef. 0.7075624
1.68	17.5			1		0.5000	56.7255	1.6931	0.0131	
							Standard Deviation	0.0048		

From R. A. Sassee Density of Triethanolammonium nitrate and LP Memorandum Report BRL-MR-3728, Dec. 1988										
TEAN Correlation		212.20		Clark's Predict. M. Volume Density						
Density	Weight	Molality	Mole Fraction	A. Molar Volume	Formula	Predict.	Predict	Residual	Error	Constant
0.99823	0.000	0.000	0		0.0000	149.1761	0.9982	0.0000	Std Err of Y Est	149.17611
1.056	0.200	1.178	0.0207658	154.431	0.1260	152.6804	1.0578	0.0018	R Squared	1.4574245
1.122	0.400	3.142	0.0535231	153.954	0.1879	154.4035	1.1209	-0.0011	No. of Observations	0.8850406
1.189	0.600	7.069	0.1128752	155.733	0.2515	156.1729	1.1872	-0.0018	Degrees of Freedom	6
1.224	0.700	10.996	0.1652228	156.563	0.2890	157.2169	1.2208	-0.0032		4
1.263	0.800	18.850	0.2533407	156.873	0.3348	158.4914	1.2533	-0.0097	X Coefficient(s)	27.822475
1.29	1.000		1	164.498	0.5000	163.0873	1.3012	0.0036	Std Err of Coef.	5.0136770
				Standard Deviation						
				0.0036						



Table II  
Density Correlation For NH3 and AN

AMMONIUM HYDROXIDE									
17.03 From CRC Handbook, 60th edition pg D-247									
Density	Weight	Molality	Mole Fraction	A. Molar Volume	Clark's Formula	Predict. M. Volume	Predict. Density	Residual Error	Regression Output:
0.99823	0.000	0.000	0	0	0.0000	25.2193	0.9982	0.0000	Constant
0.977	0.050	3.091	0.0526978	24.474	0.1867	24.5067	0.9769	-0.0001	Std Err of Y Est
0.9575	0.100	6.524	0.1050972	24.317	0.2448	24.2849	0.9577	0.0002	R Squared
0.9396	0.150	10.362	0.1572006	24.157	0.2839	24.1357	0.9398	0.0002	No. of Observations
0.9228	0.200	14.680	0.2090106	24.033	0.3137	24.0219	0.9229	0.0001	Degrees of Freedom
0.904	0.260	20.631	0.2707988	23.900	0.3423	23.9130	0.9038	-0.0002	
0.892	0.300	25.166	0.3117602	23.833	0.3583	23.8518	0.8917	-0.0003	X Coefficient(s)
						Standard Deviation	0.0002	Std Err of Coef.	
									-3.816615
									0.1967069
									25.219298
									0.0282956
									0.9894863
									6
									4
AMMONIUM NITRATE									
80.04 From CRC Handbook, 60th edition pg D-247									
Weight	Molality	Mole Fraction	Clark's Formula	0	C	10	C	25	C
0.000	0.000	0	0.0000	0.9998425	0.9997026	0.9970479	0.9922187	0.9832018	0.9718007
0.040	0.521	0.0092830	0.0879	1.0178	1.0168	1.0132	1.0079	0.9985	0.9869
0.08	1.086	0.0191797	0.1216	1.0358	1.034	1.0297	1.0238	1.0142	1.0024
0.120	1.704	0.0297530	0.1471	1.0539	1.0515	1.0464	1.04	1.0301	1.0181
0.160	2.380	0.0410749	0.1785	1.0721	1.0691	1.0633	1.0565	1.0462	1.0342
0.200	3.123	0.0532276	0.1875	1.0905	1.087	1.0806	1.0734	1.0627	1.0506
0.240	3.945	0.0663061	0.2048	1.109	1.1051	1.0982	1.0907	1.0796	1.0673
0.300	5.354	0.0879051	0.2287	1.1371	1.1327	1.1252	1.1171	1.1055	1.0931
0.400	8.329	0.1303744	0.2653	1.1862	1.181	1.1727	1.164	1.1515	1.1385
0.500	12.493	0.1835936	0.3000	1.238	1.232	1.2229	1.2136	1.2006	1.1868
AMMONIUM NITRATE									
80.04 From CRC Handbook, 60th edition pg D-247									
Weight	0	C	10	C	25	C	40	C	80
0.000	44.744	46.409	48.285	49.293	50.228	50.861	50.937	51.151	51.305
0.040	45.317	46.869	48.458	49.565	50.307	50.937	51.151	51.305	51.477
0.08	45.836	47.199	48.727	49.785	50.523	51.151	51.305	51.477	51.658
0.120	46.333	47.583	49.017	49.994	50.771	51.305	51.477	51.658	51.899
0.160	46.779	47.916	49.243	50.165	50.960	51.477	51.658	51.899	52.215
0.200	47.223	48.249	49.470	50.321	51.122	51.658	51.899	52.215	52.523
0.240	47.844	48.729	49.802	50.610	51.390	51.899	52.215	52.523	
0.300	48.613	49.339	50.218	50.907	51.664	52.215	52.523		
0.400	49.254	49.873	50.627	51.239	51.928	52.523			
0.500									

Table III  
Density of Water as a Function of Temperature

Volume	Temperature	1/Tabs	1/T2	1/t3	V-1	residual
1.0018835	-10	0.0038461	0.0000147	0.0000000	0.0018817	-0.000022
1.0007415	-5	0.0037735	0.0000142	0.0000000	0.0007412	0.0000200
1.0001575	0	0.0037037	0.0000137	0.0000000	0.0001575	0.0000208
1.0000332	5	0.0036363	0.0000132	0.0000000	0.0000332	0.0000079
1.0002974	10	0.0035714	0.0000127	0.0000000	0.0002974	-0.000004
1.0008982	15	0.0035087	0.0000123	0.0000000	0.0008982	-0.000012
1.0017961	20	0.0034482	0.0000118	0.0000000	0.0017945	-0.000014
1.0029608	25	0.0033898	0.0000114	0.0000000	0.0029564	-0.000012
1.0043688	30	0.0033333	0.0000111	0.0000000	0.0043592	-0.000006
1.0060008	35	0.0032786	0.0000107	0.0000000	0.0059829	-0.000000
1.0078423	40	0.0032258	0.0000104	0.0000000	0.0078117	0.0000054
1.0098804	45	0.0031746	0.0000100	0.0000000	0.0098319	0.0000094
1.0121054	50	0.003125	0.0000097	0.0000000	0.0120328	0.0000111
1.0145093	55	0.0030769	0.0000094	0.0000000	0.0144050	0.0000103
1.0170852	60	0.0030303	0.0000091	0.0000000	0.0169408	0.0000073
1.0198276	65	0.0029850	0.0000089	0.0000000	0.0196336	0.0000030
1.0227326	70	0.0029411	0.0000086	0.0000000	0.0224781	-0.000002
1.0257968	75	0.0028985	0.0000084	0.0000000	0.0254697	-0.000006
1.0290175	80	0.0028571	0.0000081	0.0000000	0.0286045	-0.000009
1.0323393	85	0.0028169	0.0000079	0.0000000	0.0318795	-0.000010
1.0359226	90	0.0027777	0.0000077	0.0000000	0.0352925	-0.000007
1.0396055	95	0.0027397	0.0000075	0.0000000	0.0388413	0.0000006
1.0434421	100	0.0027027	0.0000073	0.0000000	0.0425250	0.0000136

Regression Output:

Constant	-3.323745
Std Err of Y Est	0.0000126
R Squared	0.9999993
No. of Observations	23
Degrees of Freedom	18
X Coefficient (a)	0.0044057 1888.6460 -381020.7 30618111.
Std Err of Coef.	0.0000993 57.469961 11819.986 907742.43
	44.347677 32.863185 -32.23529 33.729954

Density Estimation for Mixtures of HAN, TEAN, and HNO3

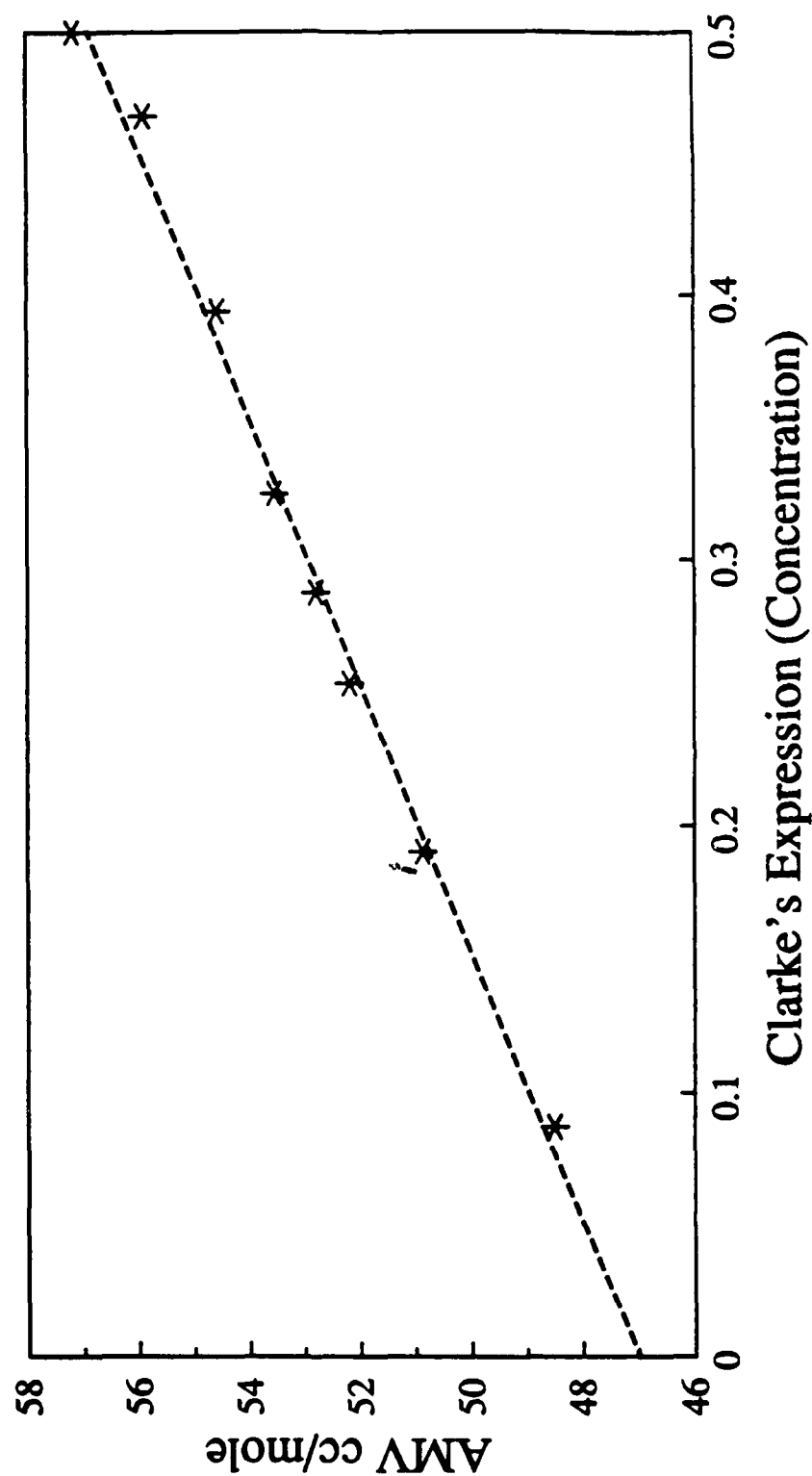
	HAN	HNO3	TEAN	H2O
Molecular Weight	96.04	63.02	212.20	18
Molality	39.164407	0	5.5955520	55.555555
Weight Fraction	0.6324773	0	0.1996559	0.1678666
Mole Fraction	0.3904	0.0000	0.0558	0.4461917
Clarke's Formula	0.4005	0.4005	0.4005	
Molar Volume	54.81	32.86	160.32	
Solution Density				1.4705
liters/1000 gm water				4.0444
Molarity	9.6836217	0	1.3835319	

Table IV  
Density Correlation for Nitric Acid

From CRC Handbook, 60th edition pg D-247

Density	HNO3	63.02	Molarity	Molality	Mole Fraction	A. Molar Volume	Clarke's Predict. Formula	Predict. M. Volume	Predict. Density	Residual Error	Constant	Std Err of Y Est	Regression Output:
0.9982071	0.000	0.000	0.000	0.000	0	29.400	0.0000	27.7452	0.9982	0.0000	0.0000	0.0000	23.074650
1.02563	0.050	0.835	0.0148101	0.0148101	0	29.557	0.1085	29.1296	1.0259	0.0002	0.0002	R Squared	1.1385855
1.0543	0.100	1.763	0.0307597	0.0307597	0	29.759	0.1492	29.6492	1.0541	-0.0002	0.0002	No. of Observations	0.9201452
1.0842	0.150	2.800	0.0479854	0.0479854	0	30.074	0.1797	30.0381	1.0834	-0.0008	0.0008	Degrees of Freedom	19
1.115	0.200	3.967	0.0666469	0.0666469	0	30.397	0.2052	30.3634	1.1139	-0.0011	0.0011		17
1.1469	0.250	5.289	0.0869313	0.0869313	0	30.715	0.2277	30.6507	1.1456	-0.0013	0.0013	X Coefficient (s)	34.869814
1.18	0.300	6.801	0.1090600	0.1090600	0	31.073	0.2483	30.9130	1.1787	-0.0013	0.0013	Std Err of Coef.	2.4914216
1.214	0.35	8.544	0.1332966	0.1332966	0	31.717	0.2675	31.1579	1.2133	-0.0007	0.0007		
1.2463	0.4	10.579	0.1599573	0.1599573	0	32.394	0.2857	31.3906	1.2495	0.0032	0.0032		
1.2783	0.45	12.983	0.1894249	0.1894249	0	33.082	0.3032	31.6146	1.2875	0.0092	0.0092		
1.31	0.5	15.868	0.2221673	0.2221673	0	33.900	0.3204	31.8329	1.3272	0.0172	0.0172		
1.3393	0.55	19.394	0.2587626	0.2587626	0	34.764	0.3372	32.0475	1.3689	0.0296	0.0296		
1.3667	0.6	23.802	0.2999333	0.2999333	0	35.692	0.3539	32.2605	1.4127	0.0460	0.0460		
1.3913	0.65	29.469	0.3465947	0.3465947	0	36.640	0.3706	32.4736	1.4587	0.0674	0.0674		
1.4134	0.7	37.025	0.3999238	0.3999238	0	37.564	0.3874	32.6884	1.5069	0.0935	0.0935		
1.4337	0.75	47.604	0.4614595	0.4614595	0	38.466	0.4045	32.9068	1.5575	0.1238	0.1238		
1.4521	0.8	63.472	0.5332543	0.5332543	0	39.343	0.4220	33.1305	1.6105	0.1584	0.1584		
1.4686	0.85	89.919	0.6181068	0.6181068	0	40.215	0.4402	33.3615	1.6660	0.1974	0.1974		
1.4826	0.9	142.812	0.7199360	0.7199360	0	41.103	0.4590	33.6022	1.7240	0.2414	0.2414		
1.4932	0.95	301.492	0.8444027	0.8444027	0		0.4789	33.8556	1.7843	0.2911	0.2911		
1.5129	1				1		0.5000	34.1252					

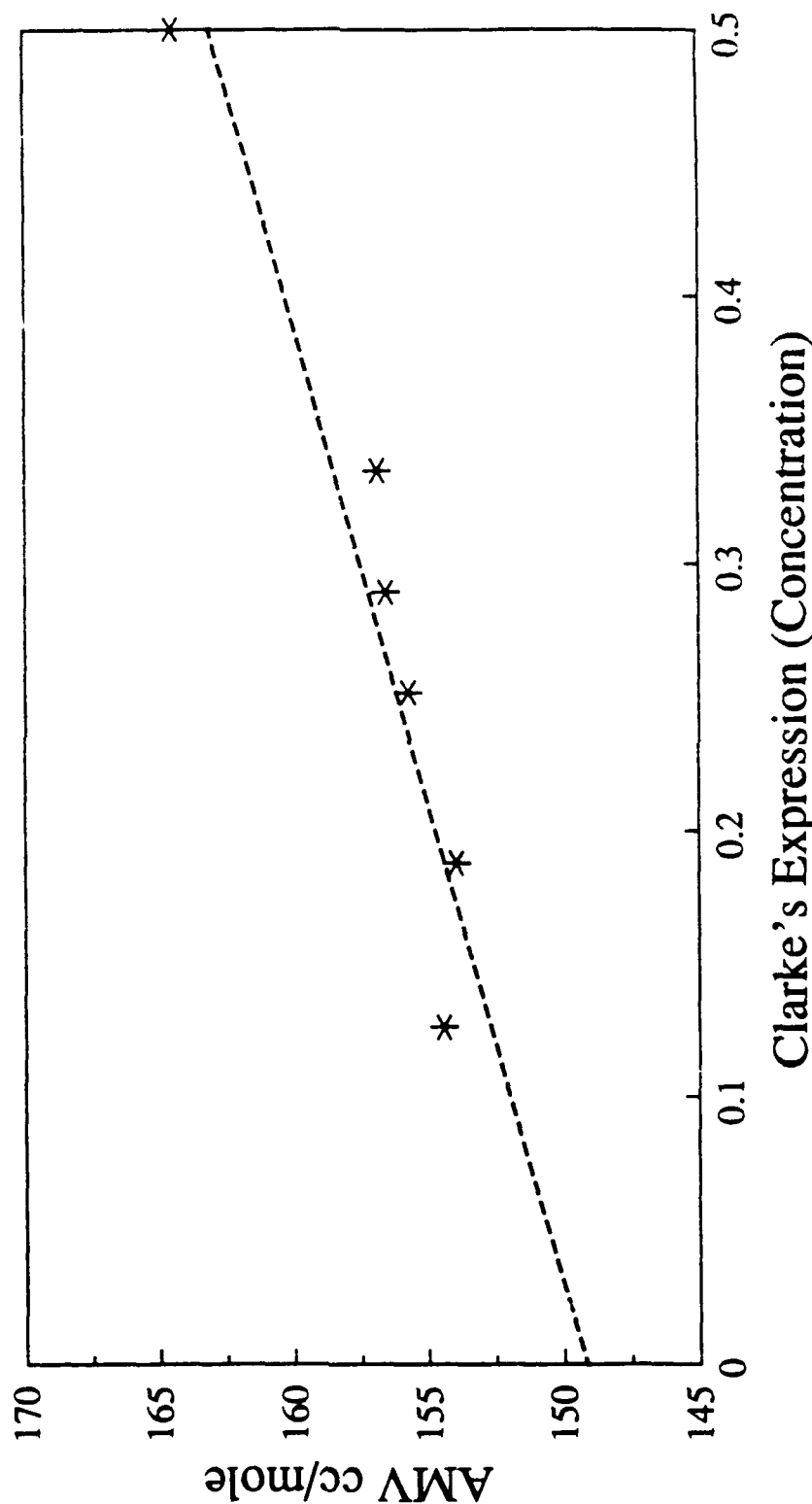
**Figure 1**  
**HAN**  
 Apparent Molar Volume At 20 C



Original Data from SASSE et al  
 Density of Hydroxylammonium Nitrate Solutions  
 Memorandum Report BRL-MR-3720, December, 1988

Intercept: 46.97 Slope: 19.83  
 R-square: .993

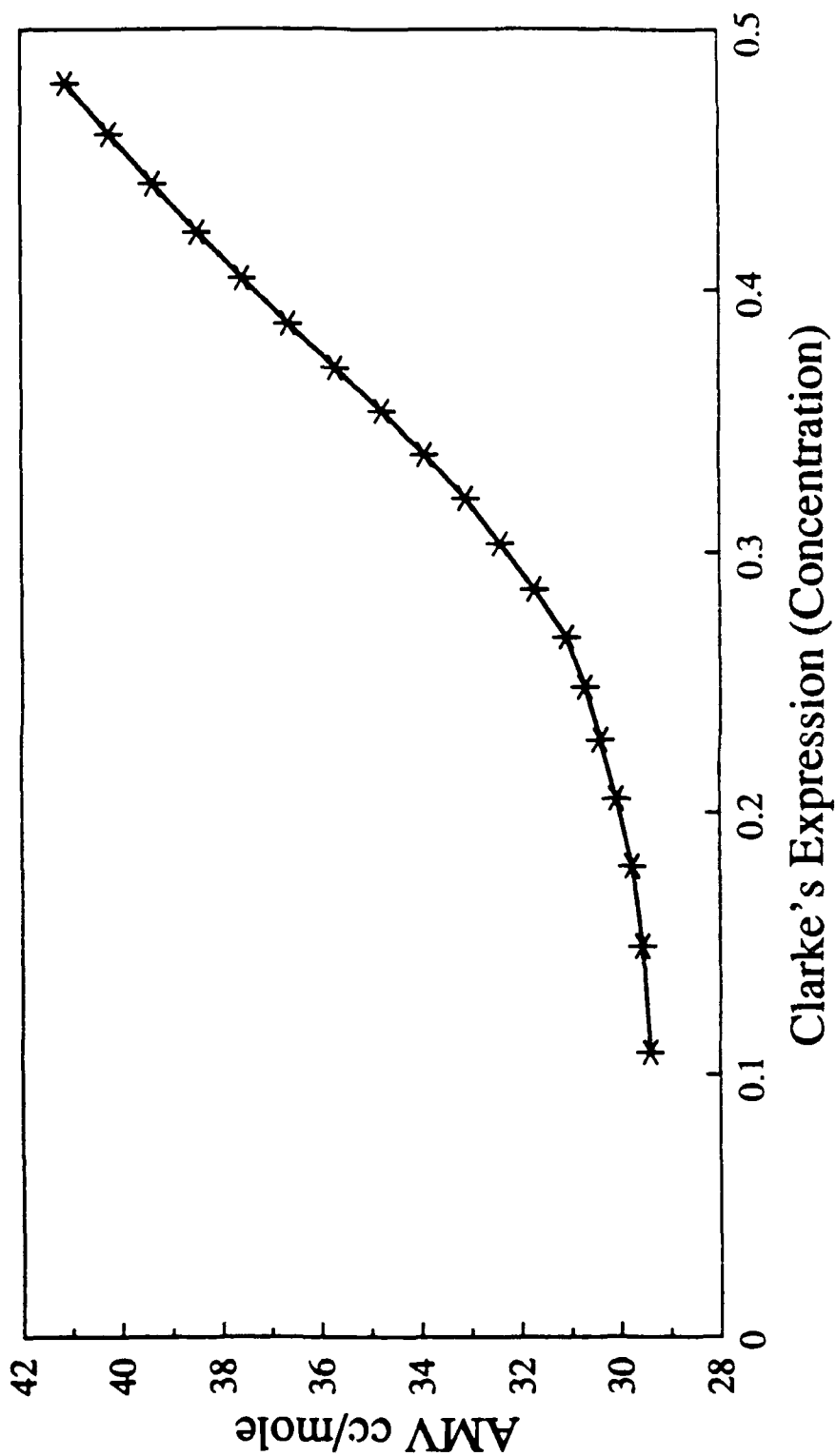
**Figure 2**  
**TEAN**  
**Apparent Molar Volume at 20 °C**



From R. A. Sassee  
 Density of Triethanolammonium nitrate and LP  
 Memorandum Report BRL-MR-3728, Dec. 1988

Intercept: 149.2 Slope: 27.8  
 R-square: .885

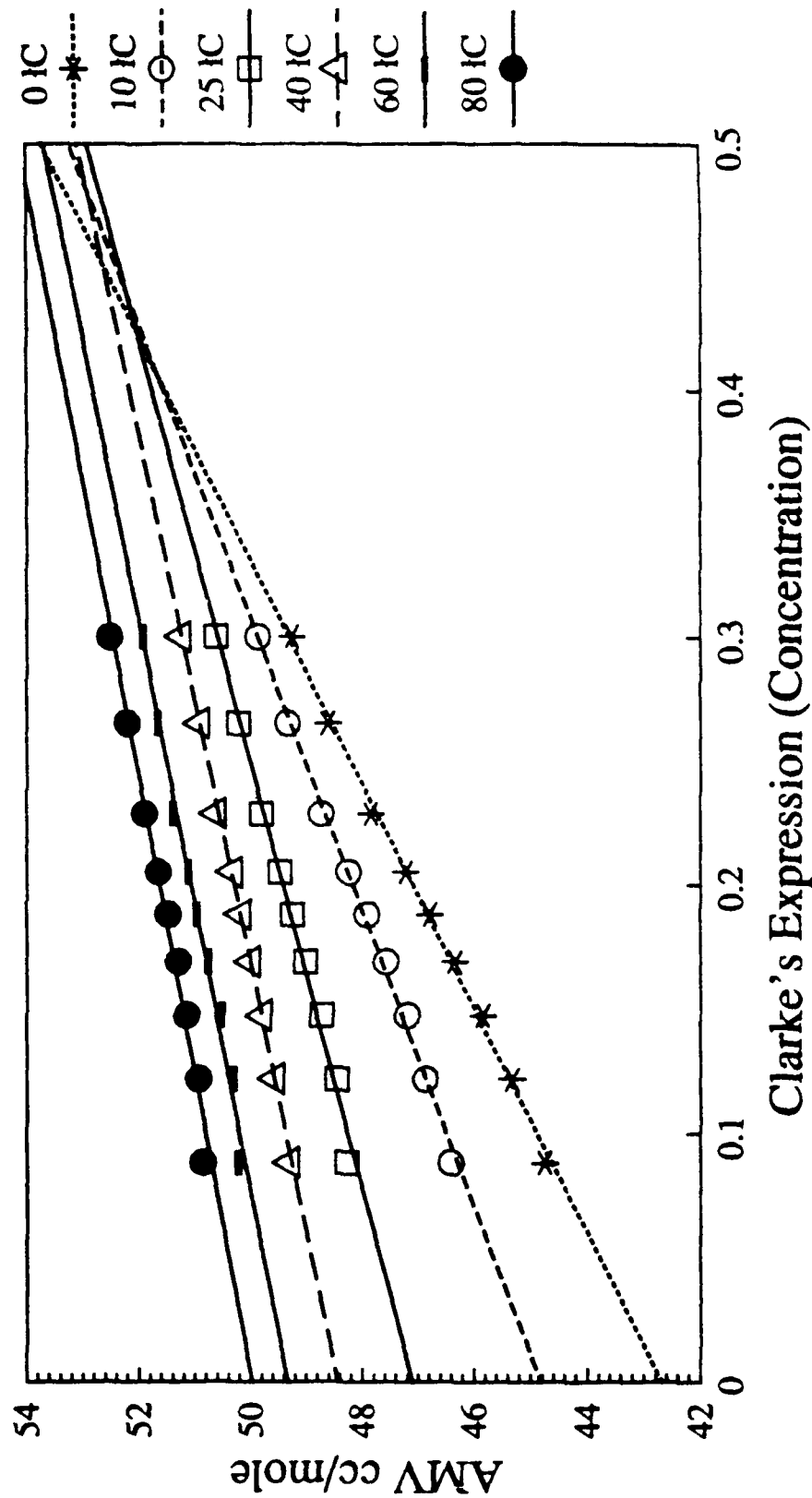
**Figure 3**  
**HNO<sub>3</sub>**  
 Apparent Molar Volume at 20 C



No Regression Attempted  
 Assume V' is 29.5 for low concentrations

From CRC Handbook, 60th edition pg D-247

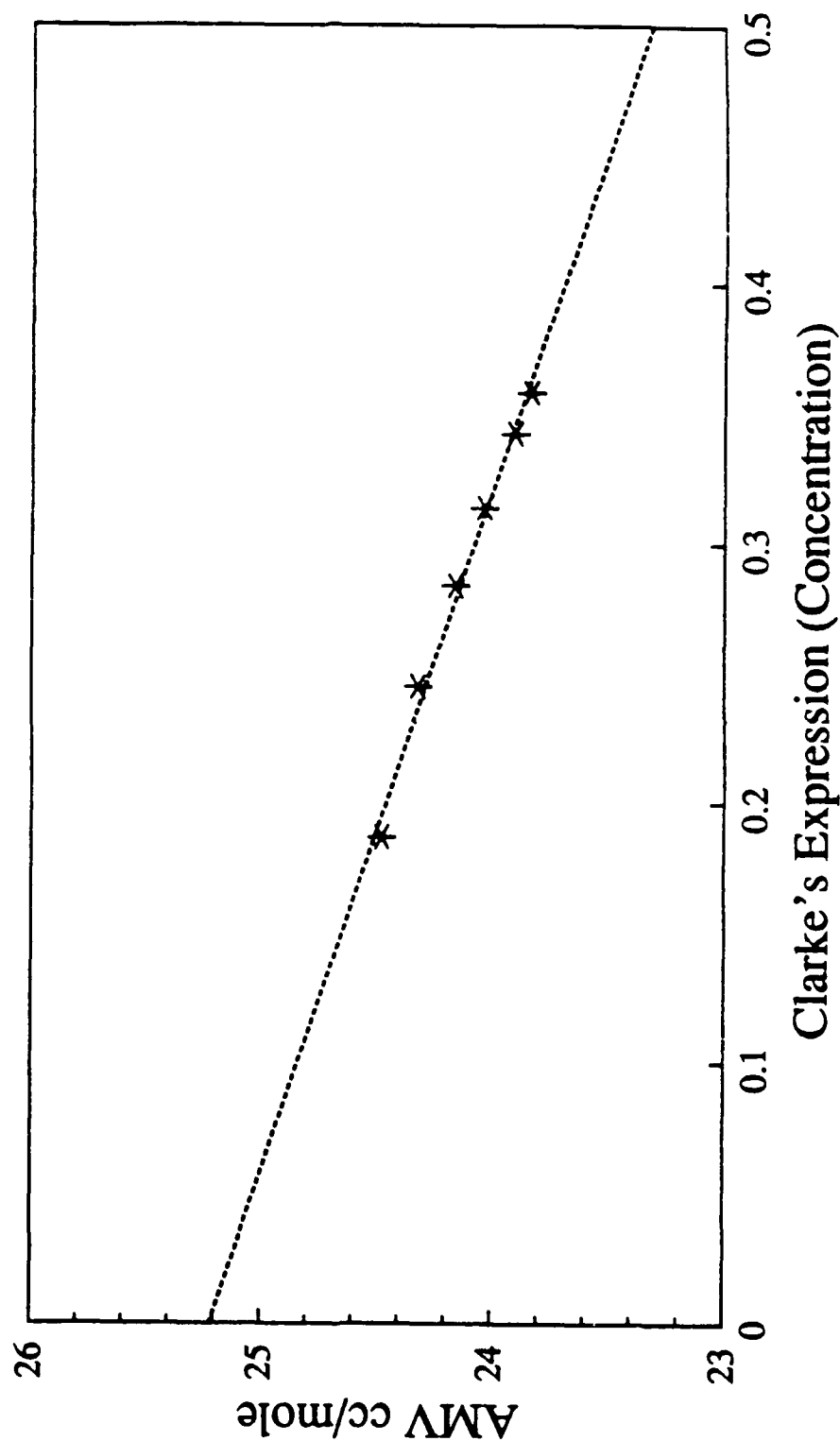
**Figure 4**  
**Ammonium Nitrate**  
**Apparent Molar Volume at Various Temperatures**



R-square is >.99 for all but data at 0 C

From CRC Handbook, 60th edition pg D-247

**Figure 5**  
**Ammonia**  
**Apparent Molar Volume at 20 tC**

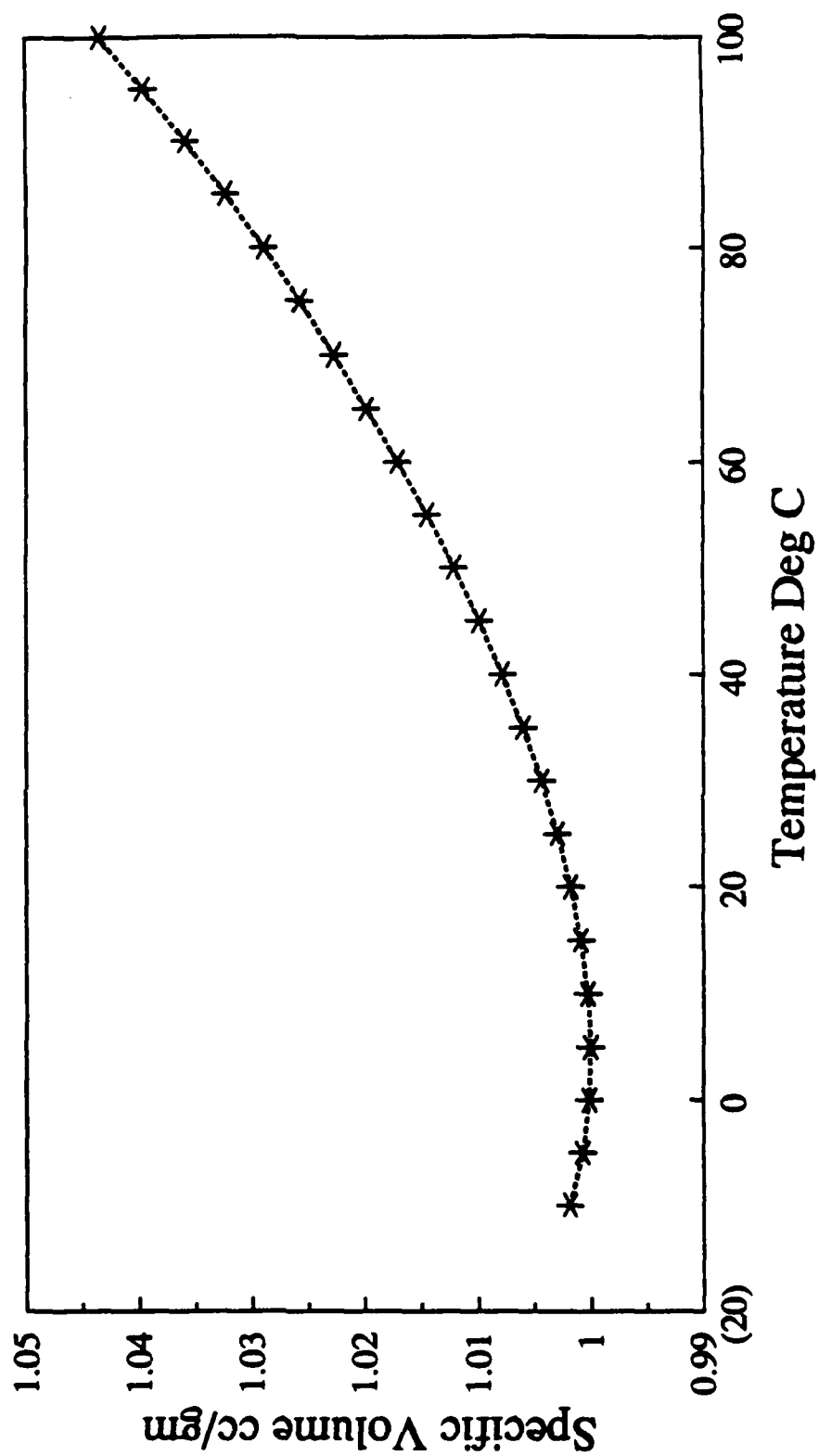


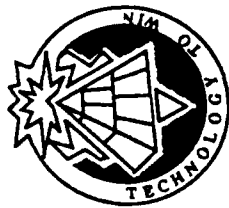
Intercept: 25.22 Slope: -3.81  
 R-square: .989

From CRC Handbook, 60th edition pg D-247

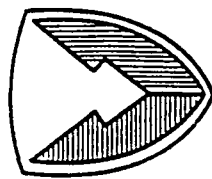


**Figure 6**  
**Water**  
**Specific Volume Vs Temperature**





BALLISTIC RESEARCH LABORATORY



US ARMY  
LABORATORY COMMAND

# *Investigation of FTIR Techniques for Determination of Ammonium Nitrate, Hydroxylamine, and Nitric Acid in Aqueous HAN*

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*5th Conf. on HAN-Based Liquid Propellant Structure & Properties,  
BRL, 22-23 Aug 1989*

## *Acknowledgement*

One of the authors (G. Singh) acknowledges the summer support of the BRL to conduct this investigation.

# *Background*

PREVIOUS WORK AT THE BRL (FIFER, 1984\*) SHOWED THAT ALL COMPONENTS OF HAN-BASED LPs (H<sub>2</sub>O, HA+, N-, TEA+ OR IPA+) COULD BE DETERMINED RAPIDLY (60-90 sec) AND NON-DESTRUCTIVELY USING FTIR-CYLINDRICAL INTERNAL REFLECTION (FTIR-CIR) TECHNIQUES.

## ADVANTAGES:

- ALL SPECIES MEASURED SIMULTANEOUSLY WITH SINGLE TECHNIQUE.
- COMPATIBLE WITH ON-LINE PROCESS CONTROL/ANALYSIS

\*1984 JANNAF PROPELLANT CHARACTERIZATION SUBCOMMITTEE  
MEETING, CPIA PUB. 413, 205-214, JAN 1985.

## *Objective*

TO DETERMINE IF FTIR TECHNIQUES  
CAN ALSO BE USED TO DETERMINE  
AMMONIUM NITRATE (AN), "FREE"  
HYDROXYLAMINE (HA), AND "EXCESS"  
NITRIC ACID IN AQUEOUS HAN (AND LPS)

PROGRESS REPORT: STUDY BEGAN JUNE 1989

# *Relevance to HAN Manufacturing Process*

A. AMMONIUM NITRATE: CAN BE PRODUCED ALONG WITH HAN IF ELECTROCHEMICAL PROCESS DOES NOT PROCEED IDEALLY. CURRENT ANALYTICAL PROCEDURE: ADD BASE, COLLECT EVOLVED AMMONIA GAS IN BORIC ACID, TITRATE.

B. HYDROXYLAMINE: RESIN TECHNOLOGY BEING INVESTIGATED FOR REMOVAL OF "EXCESS" NITRIC ACID CAN LEAD TO FORMATION /ADDITION OF "FREE" (NON-IONIC) HYDROXYLAMINE (HA). CURRENTLY NO ANALYTICAL PROCEDURE FOR HA.

C. NITRIC ACID: DURING ELECTROCHEMICAL PRODUCTION OF HAN, ~3 M HAN PRODUCED WITH ~0.5 M "EXCESS" ACID. CURRENT ANALYTICAL PROCEDURE: TITRATION.

## *Approach*

- ▶ MEASURE FTIR (AND UV/VIS) SPECTRA FOR HAN SOLUTIONS WITH ADDED AMMONIUM NITRATE (AN), NaOH {TO PRODUCE HYDROXYLAMINE (HA)} , OR NITRIC ACID (HN)
- ▶ LOOK FOR SPECTRAL FEATURES THAT MIGHT BE USABLE FOR SPECTROSCOPICALLY MEASURING AN, HA, AND HN IN AQUEOUS HAN.

# *Experimental Techniques*

## ► *Instrumentation:*

A. MATTSON POLARIS FTIR WITH DTGS DETECTOR

COADD 100 INTERFEROGRAMS AT 4  $\text{cm}^{-1}$  RESOLUTION

RANGE: 400 to 7800  $\text{cm}^{-1}$

"MIR": 400 - 4000  $\text{cm}^{-1}$

"NIR": 4000 - 7800  $\text{cm}^{-1}$  (NOT OPTIMIZED FOR NIR)

B. PERKIN ELMER LAMBDA 3840 DIODE ARRAY UV/VIS  
SPECTROMETER

32 SCANS COADDED AT 0.25 nm RESOLUTION

RANGE: 200 TO 900 nm (50,000 to 11,110  $\text{cm}^{-1}$ )



# Experimental Techniques

## Cells

TYPE, MATERIALS	REGION	PATH (microns)	RANGE (cm <sup>-1</sup> )
1. ATR, "CIRCLE", ZnSe ROD	MIR	10 a	>650
2. TRANSM, ThBr1 WINDOWS*	MIR	100	>400
3. TRANSM, ZnS WINDOWS#	MIR	100	>700
4. TRANSM, CaF2 WINDOWS	NIR	100	>1000
5. TRANSM, QUARTZ	NIR	500,1000	>2300
6. TRANSM, QUARTZ	UV	10000	<50,000 (> 200 nm)

a EQUIVALENT PATHLENGTH FOR TRANSMISSION CELL

\* KRS-5

# IRTRAN 2

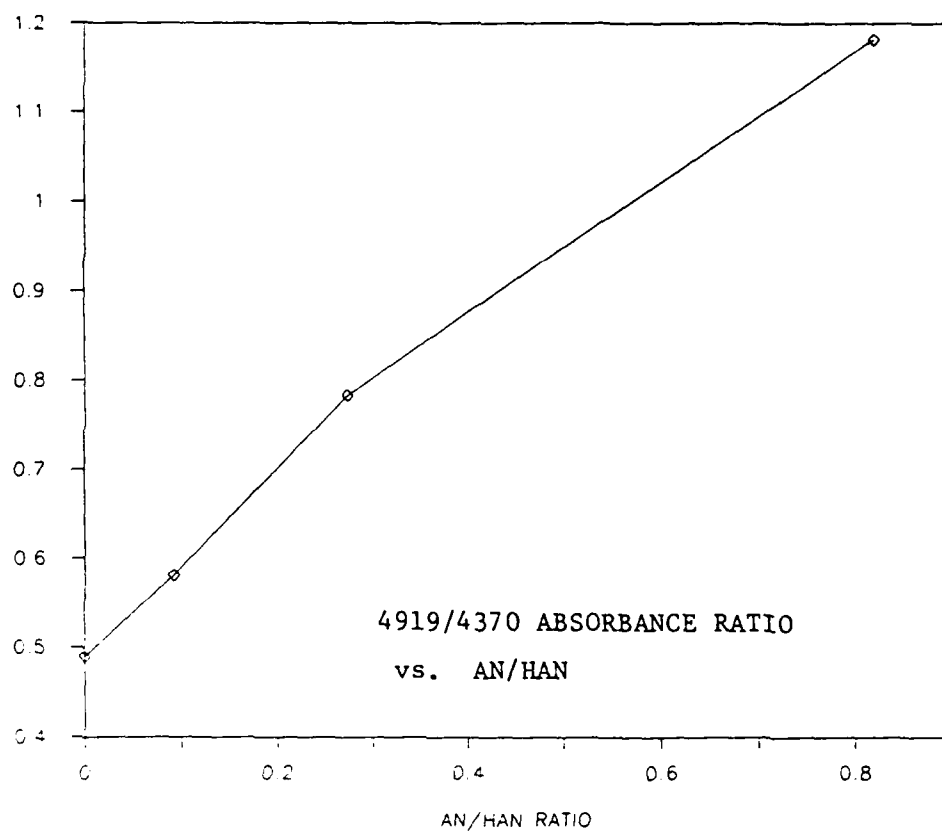
# ***A. Ammonium Nitrate (AN) in HAN***

# *A. Ammonium Nitrate (AN) in HAN, Solutions Investigated*

MIXTURE	MOLARITY		MOLAR RATIO AN/HAN
	AN	HAN	
HAN (13.00 M)	0.0	13.00	0.0
AN + HAN (1:9)	1.065	11.70	0.0910
AN + HAN (1:3)	2.660	9.750	0.2731
AN + HAN (1:1)	5.325	6.500	0.8190
AN (10.65 M)	10.65	0.0	$\infty$

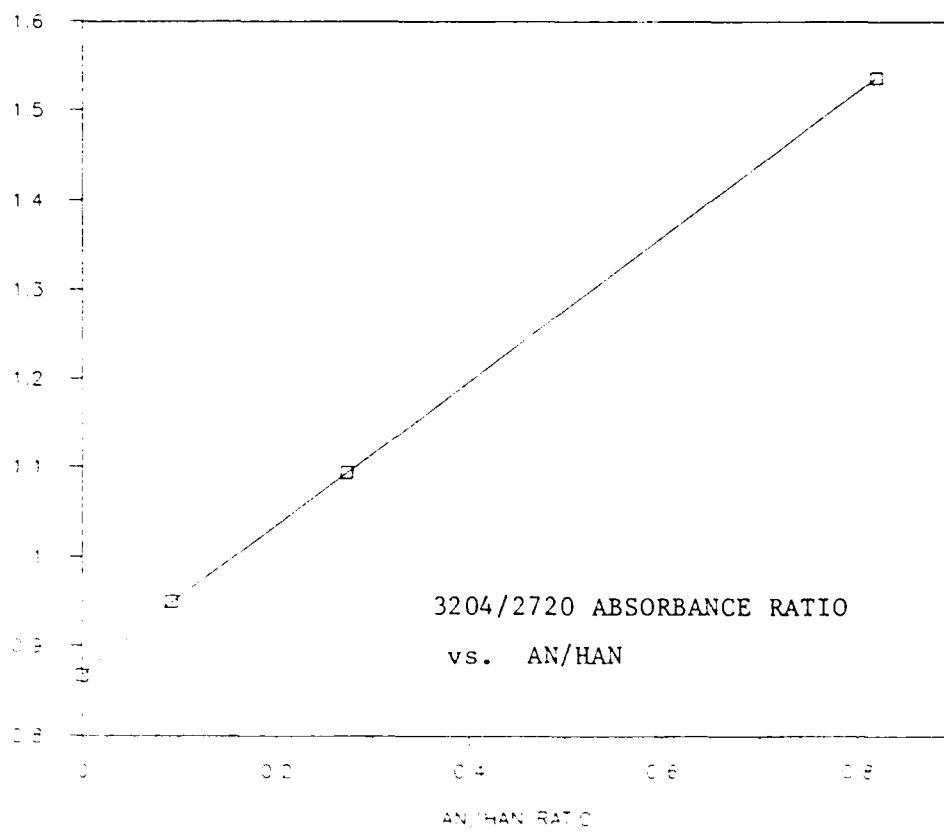
# NIR CORRELATION FOR AN/HAN

ABS RATIO 4919/4370



# MIR CORRELATION FOR AN/HAN

ABS. RATIO 3204/2720



## *B. Hydroxylamine (HA) in HAN*

## *B. Hydroxylamine (HA) in HAN, Solutions Investigated*

MIXTURE	MOLARITY		MOLAR RATIO#
	HA	HAN	HA/HA+
50:50 13 M HAN:H <sub>2</sub> O	0.0	6.50	0.0
50:50 13 M HAN:2 M NaOH	1.00	5.50	0.182
50:50 13 M HAN:4 M NaOH	2.00	4.50	0.444
25:75 13 M HAN:4 M NaOH*	3.00	0.25	12.0

# CALCULATED ASSUMING NO NITRIC ACID (OR AN) IN THE HAN

\* SOME BUBBLING OBSERVED

(BASE (NaOH) NEUTRALIZED HYDROXYLAMMONIUM CHLORIDE ("HAC") SOLUTIONS WERE ALSO EMPLOYED)

## *C. Nitric Acid (HN)* *in HAN*



## ***C. Nitric Acid (HN) in HAN, Solutions Investigated***

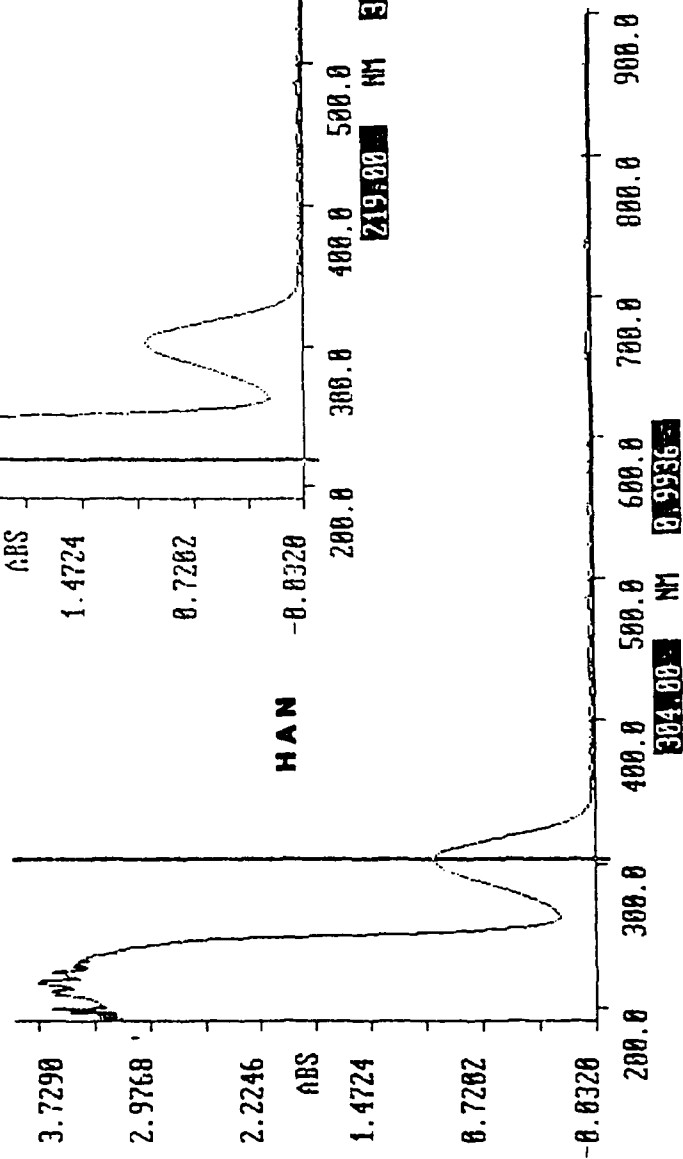
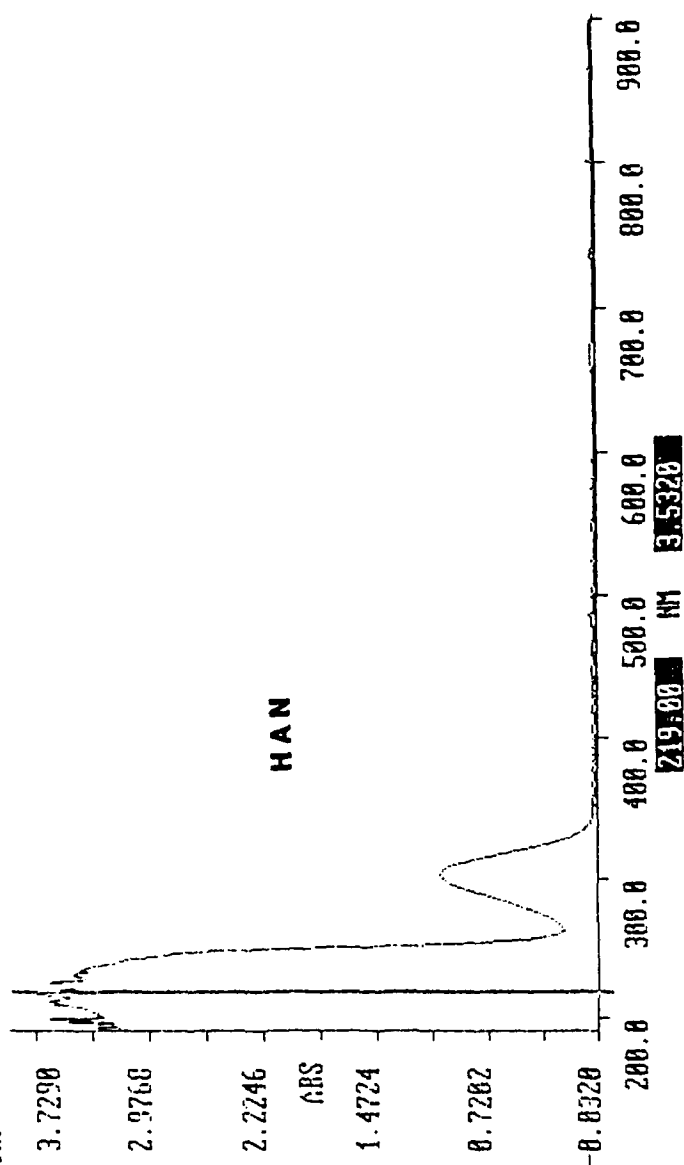
▶ 0.269 N HN

▶ 1.00 N HN

▶ 3.25 M HAN WITH 0.75 N HN

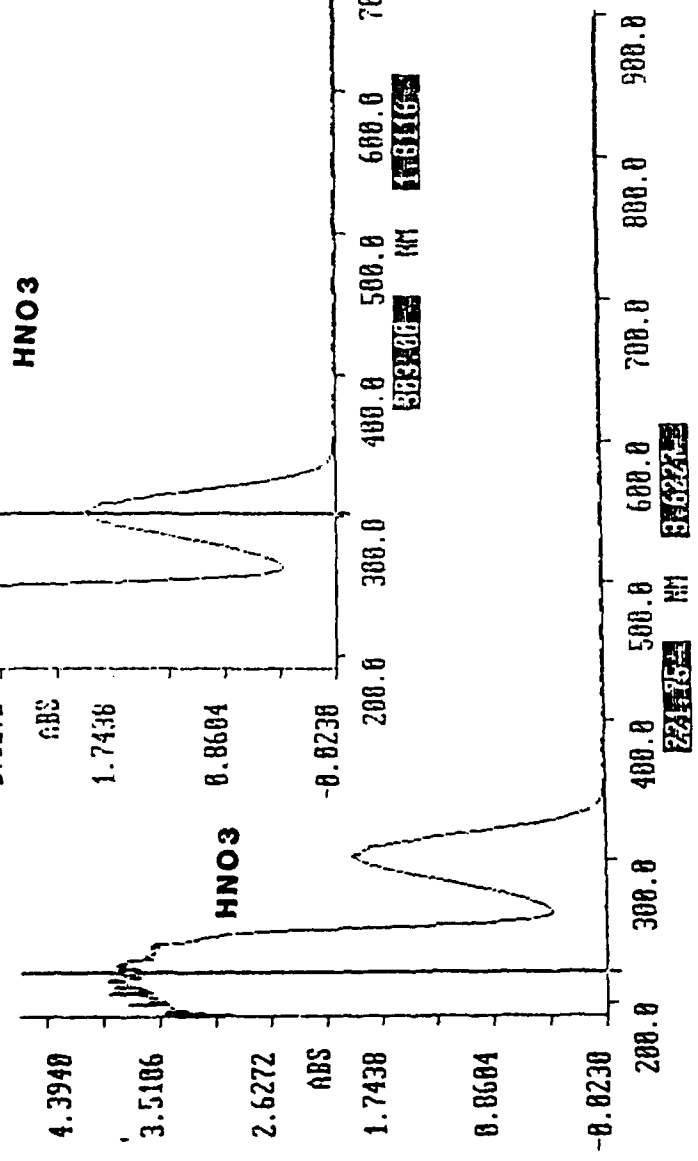
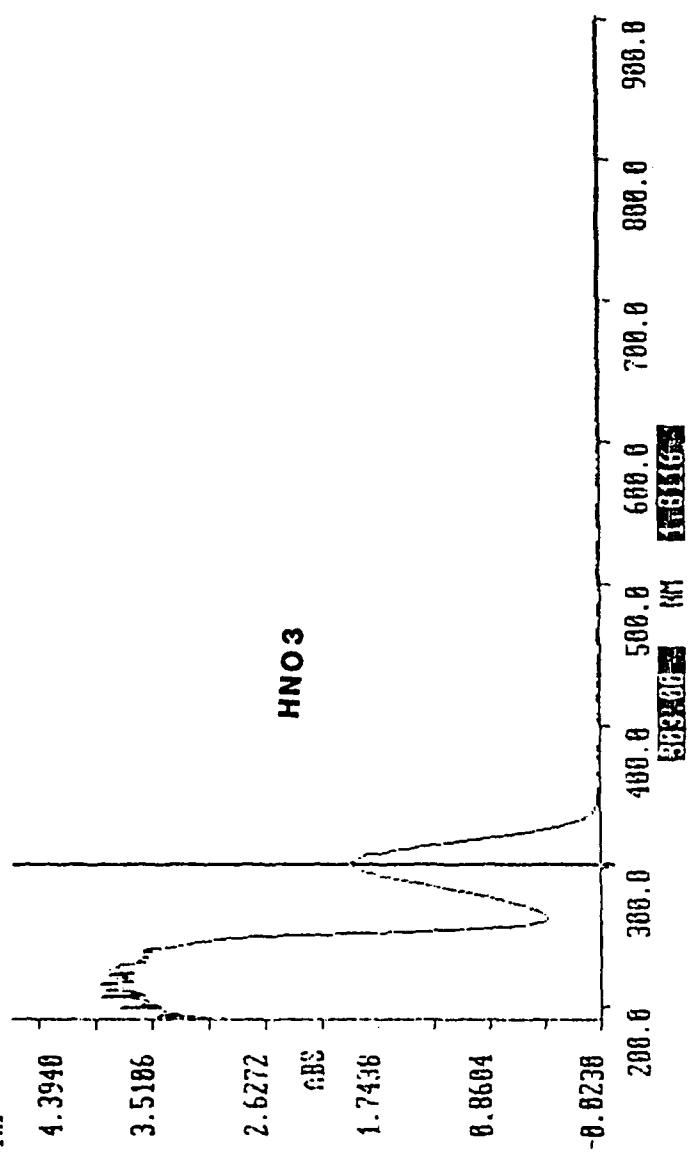
X: abs 900.0-190.0; pts 2841; int 0.25; ord -0.03-3.729; A AC 32

inf:



X: ; abs 900.0-196.0; pts 2841; int 0.25; ord -0.02-4.394; A AC 32

inf:



## *Summary A. Ammonium Nitrate (AN) in HAN*

► THE AMMONIUM ION ( $\text{A}^+$ ) HAS PROMINENT SPECTRAL FEATURES IN BOTH THE MID- AND NEAR-IR REGIONS:

MIR: 3204  $\text{cm}^{-1}$

NIR: 4919  $\text{cm}^{-1}$

► SINCE THESE ARE SUPERIMPOSED ON HYDROXYLAMMONIUM ION ( $\text{HA}^+$ ) BANDS, AN ABSORBANCE RATIO FOR EITHER OF THESE BANDS RELATIVE TO A BAND DUE ONLY TO  $\text{HA}^+$  APPEARS TO PROVIDE A SENSITIVE (AND CONCENTRATION-INDEPENDENT) TEST FOR THE  $\text{AN}/\text{HA}^+$  RATIO.

MIR: 3204/2720 or 3204/1005

NIR: 4919/4370

► RELATIVELY SMALL AMOUNTS (PERHAPS 1% OR LESS RELATIVE TO HAN) OF AN CAN BE DETECTED WITH EITHER THE MIR OR NIR TECHNIQUE. FURTHER WORK WILL BE REQUIRED TO DETERMINE DETECTION LIMITS AND MEASUREMENT ACCURACY.

## *Summary B.* *Hydroxylamine (HA) in HAN*

► UNIQUE BANDS DUE TO HA HAVE BEEN IDENTIFIED IN BOTH THE MID- AND NEAR-IR REGIONS. THE PRINCIPAL BANDS ARE:

	BAND (cm-1)	SUITABLE PATHLENGTH (MICRONS)
MIR:	910	100-200
	(1190)	(COINCIDENT WITH HA+ BAND)
NIR:	6420	1000-5000
	(4920)	(ON STEEP PORTION OF WATER BAND)
	4635	500-1000
	4517	500-1000

► THESE HA BANDS ARE WEAK COMPARED TO THE HA+ BANDS. CONSEQUENTLY, LONGER PATHLENGTH CELLS ARE NEEDED THAN FOR HAN/LP PRINCIPAL INGREDIENT ANALYSIS. (10 MICRON CIRCLE CELL "PATHLENGTH" NOT SUITABLE).

► DETECTION LIMITS FOR HA MAY NOT BE AS LOW AS FOR AN.

## ***Summary C. Nitric Acid (HN) in HAN***

► **NO SUCCESS TO DATE; ONLY TWO BANDS HAVE BEEN OBSERVED FOR HN:**

**MIR: 1300-1400 cm<sup>-1</sup>**

**NIR: none**

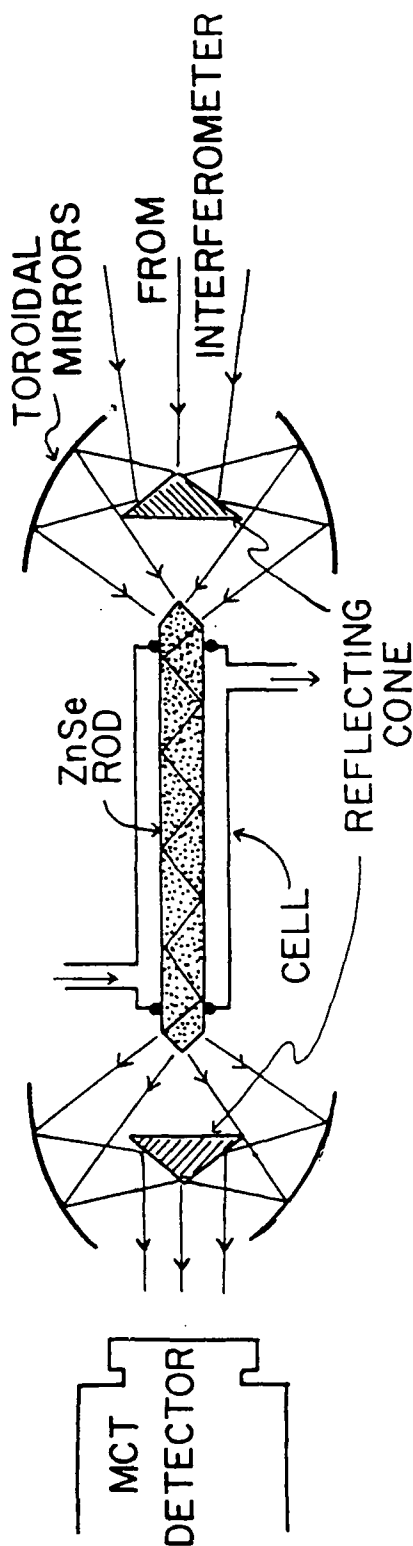
**UV: 303 nm (33,000 cm<sup>-1</sup>)**

► **BOTH OF THESE BANDS APPEAR TO BE IDENTICAL TO THOSE FOR THE NITRATE ANION (N<sup>-</sup>), PRESUMABLY BECAUSE HN EXISTS IN AQUEOUS SOLUTION PRIMARILY AS NITRATE [NO<sub>3</sub>]<sup>-</sup> AND HYDRATED PROTONS [H(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup>, WITH THE HYDRATED PROTONS APPARENTLY NOT CONTRIBUTING ANY NEW SPECTRAL FEATURES.**

## *Summary - Overall*

- ▶ SPECTRAL FEATURES IN THE MID- AND NEAR-IR HAVE BEEN IDENTIFIED FOR BOTH AMMONIUM NITRATE (AN) AND HYDROXYLAMINE (HA) IN AQUEOUS HAN USING FTIR TECHNIQUES. THIS SHOULD PERMIT DEVELOPMENT OF SPECTRAL-BASED ANALYTICAL TECHNIQUES FOR BOTH SPECIES, IN EITHER THE MID- OR NEAR-IR REGIONS.
- ▶ ANALYSIS OF HA APPEARS TO REQUIRE LONGER PATHLENGTHS THAN FOR AN.
- ▶ NO SPECTROSCOPIC TECHNIQUES HAVE BEEN IDENTIFIED FOR ANALYSIS OF NITRIC ACID (HN) IN HAN.

## CYLINDRICAL INTERNAL REFLECTION

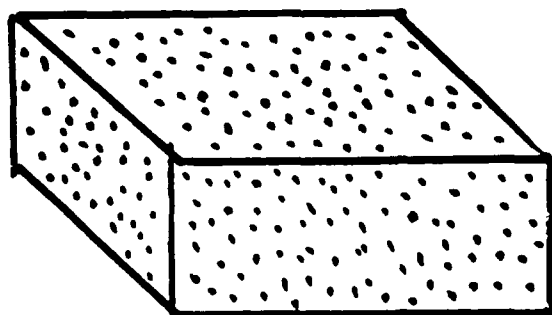


### cylindrical internal reflection: \*

LIGHT REFLECTING INSIDE A SOLID ZINC SELENIDE ROD "PICKS UP" ABSORPTIONS FROM THE LIQUID IN CONTACT WITH IT. ADVANTAGE: NOT NECESSARY TO MAINTAIN VERY SMALL (~5 MICRON) PATHLENGTH BETWEEN TWO SALT WINDOWS AS IN TRANSMISSION TECHNIQUES. A VARIATION OF "ATTENUATED TOTAL REFLECTION" (ATR)

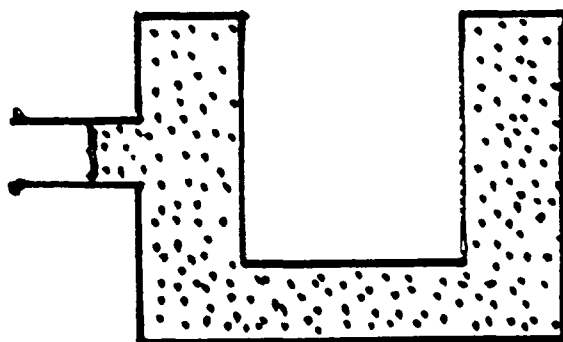
\* A. REIN AND P. WILKS, JR., "CYLINDRICAL INTERNAL REFLECTION CELL", AMERICAN LABORATORY, VOL. 14, NO. 10, P.152-155 (1982)





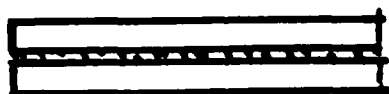
1 cm

CELLS



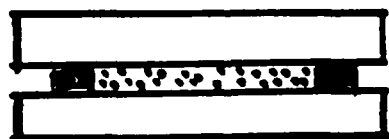
0.5 mm

QUARTZ



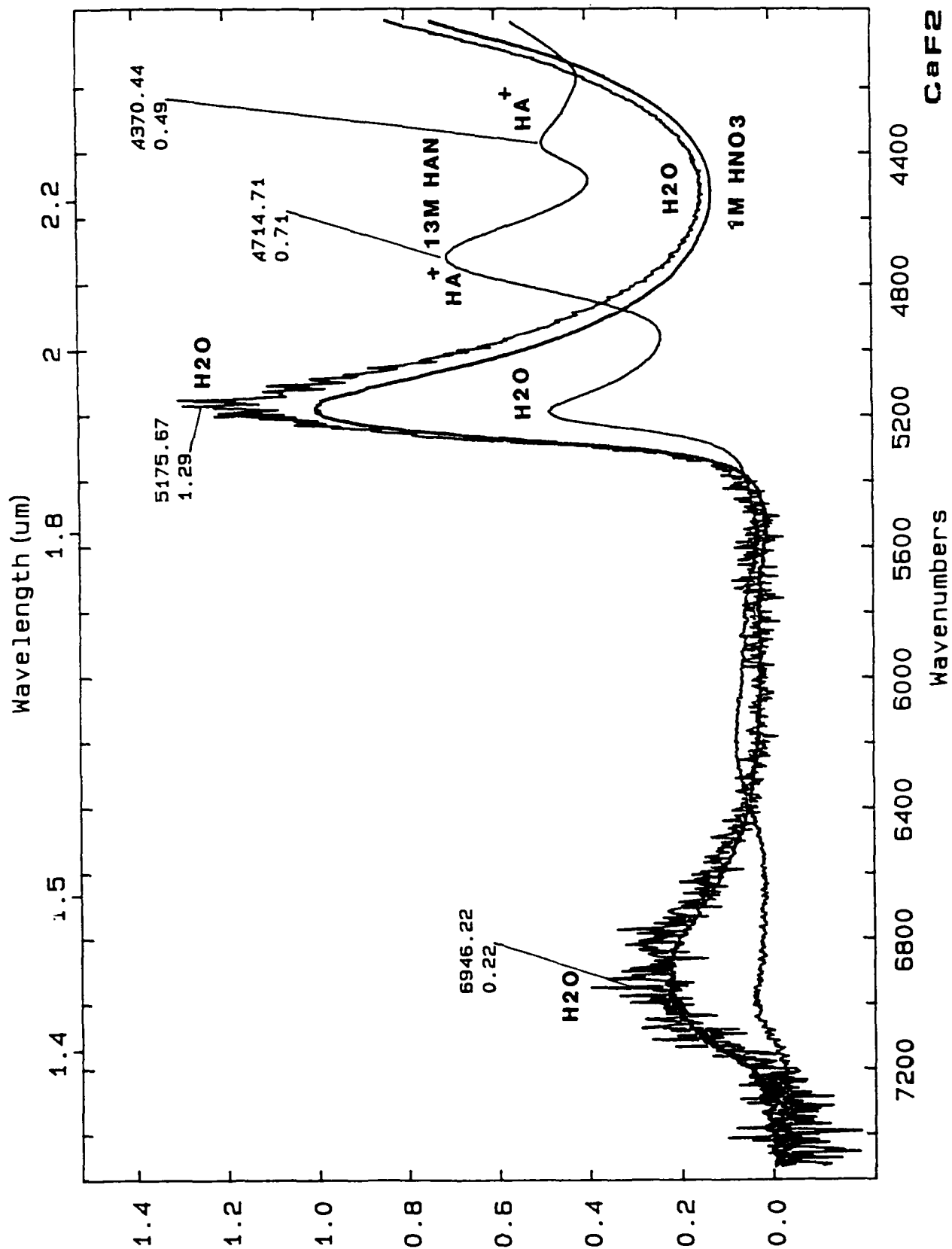
?

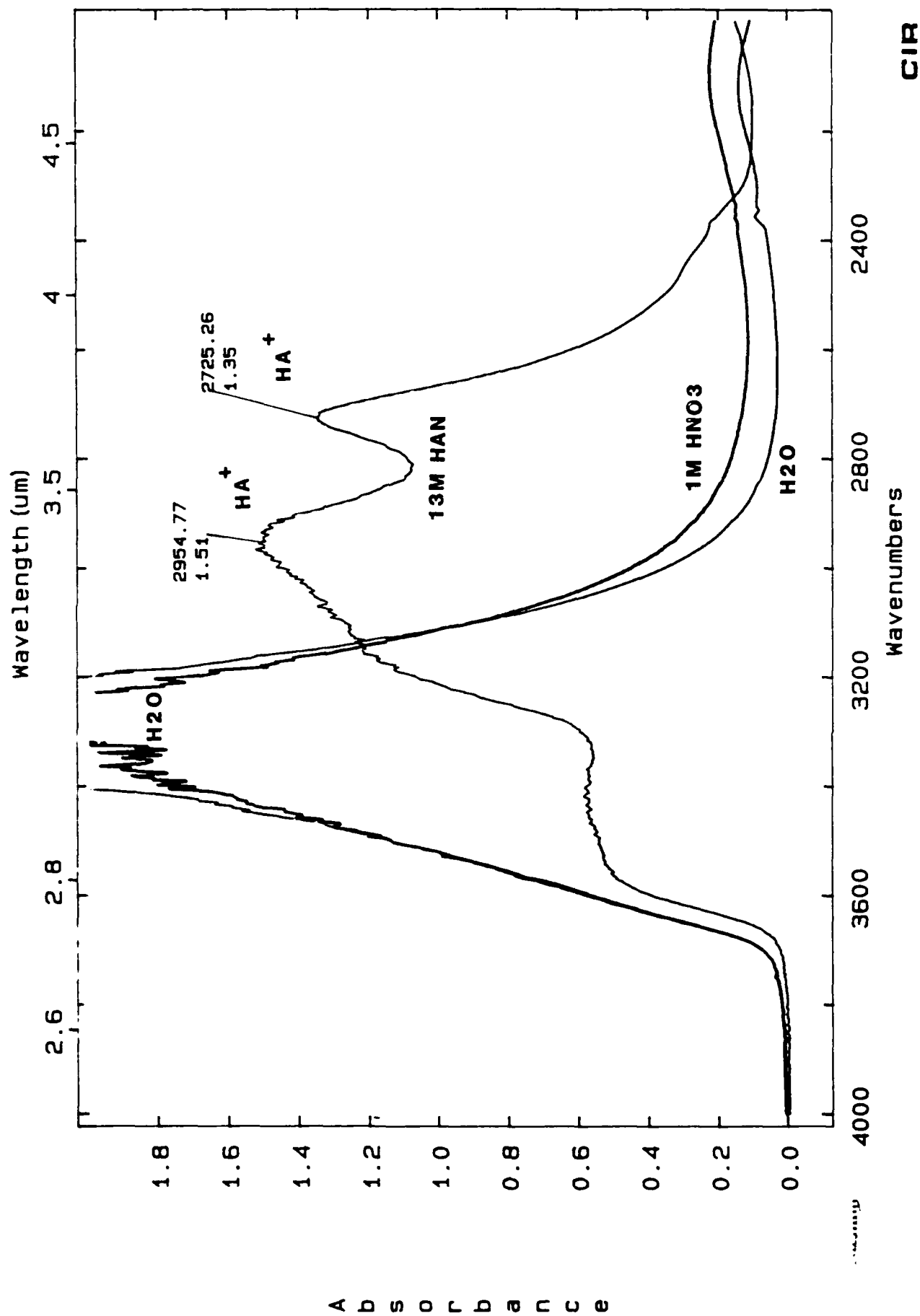
ZnS



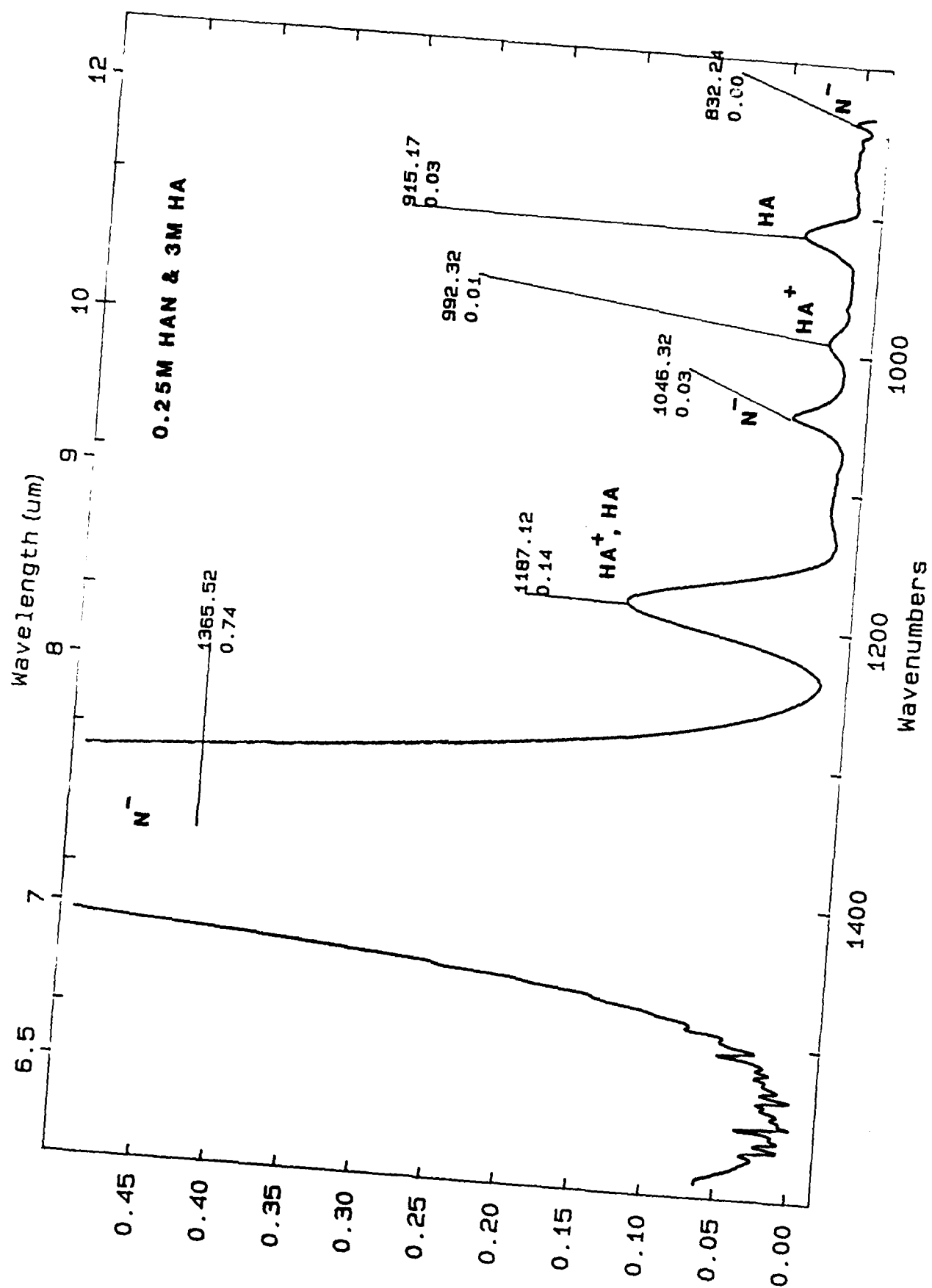
~100  $\mu$

CaF<sub>2</sub>

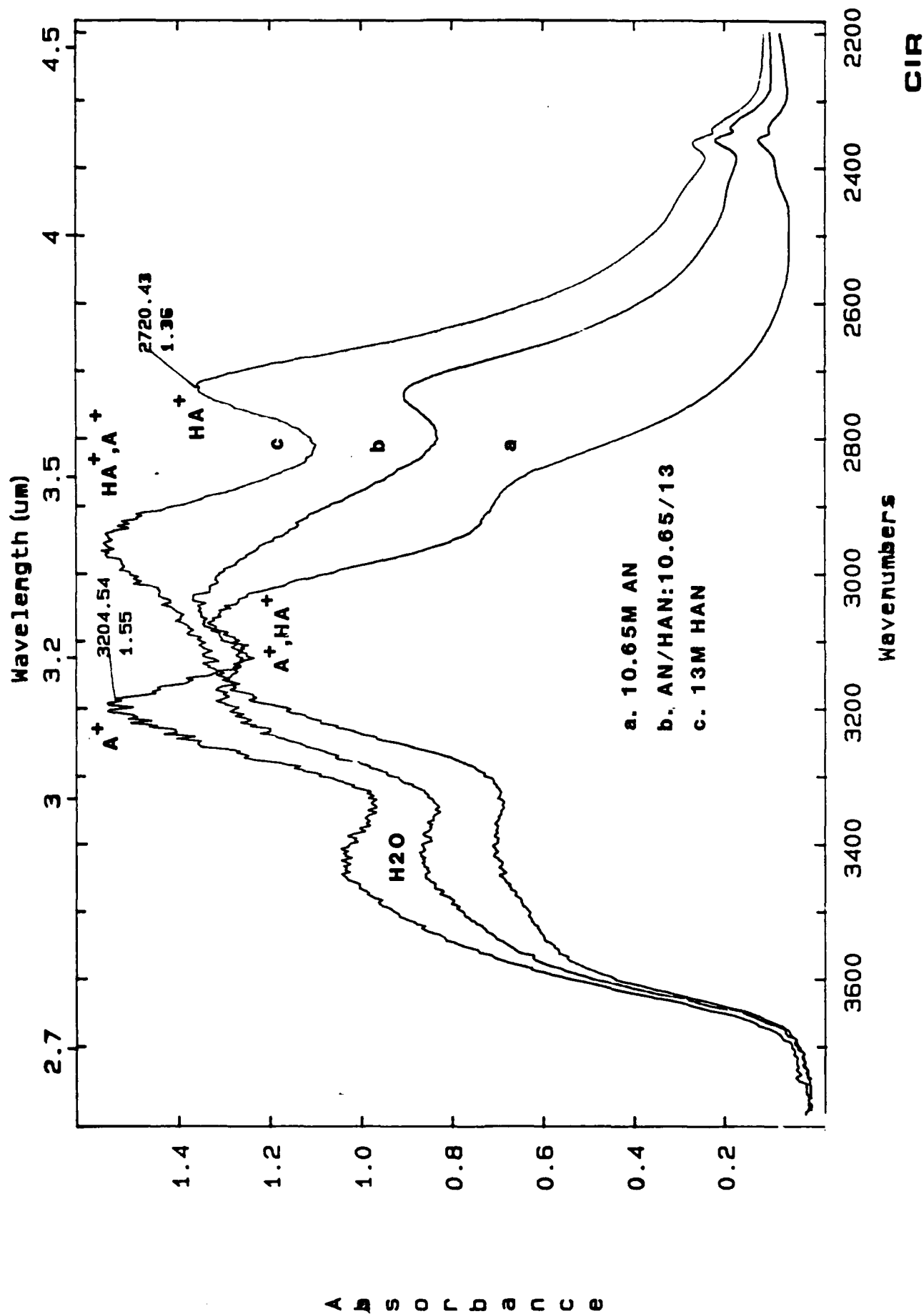


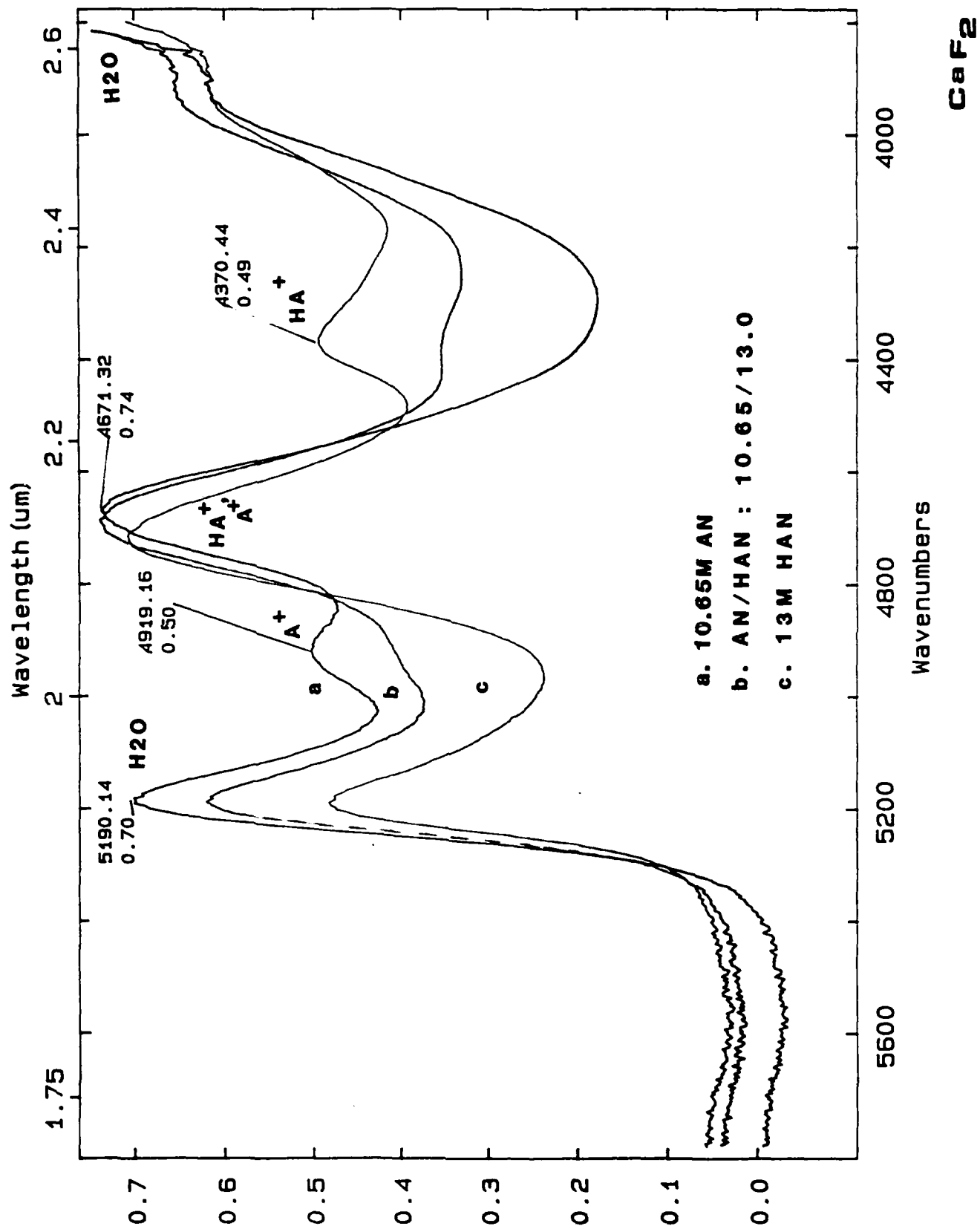


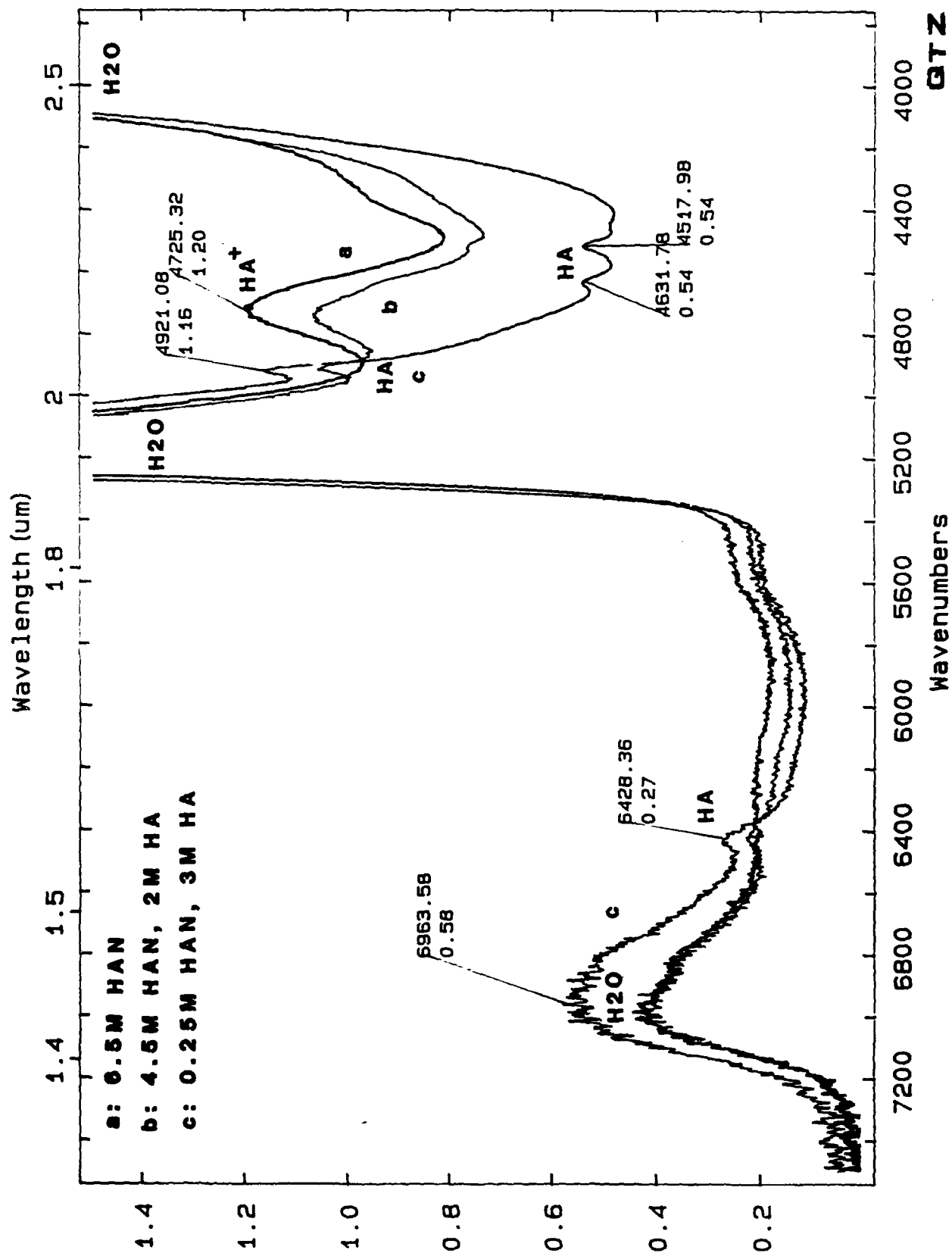




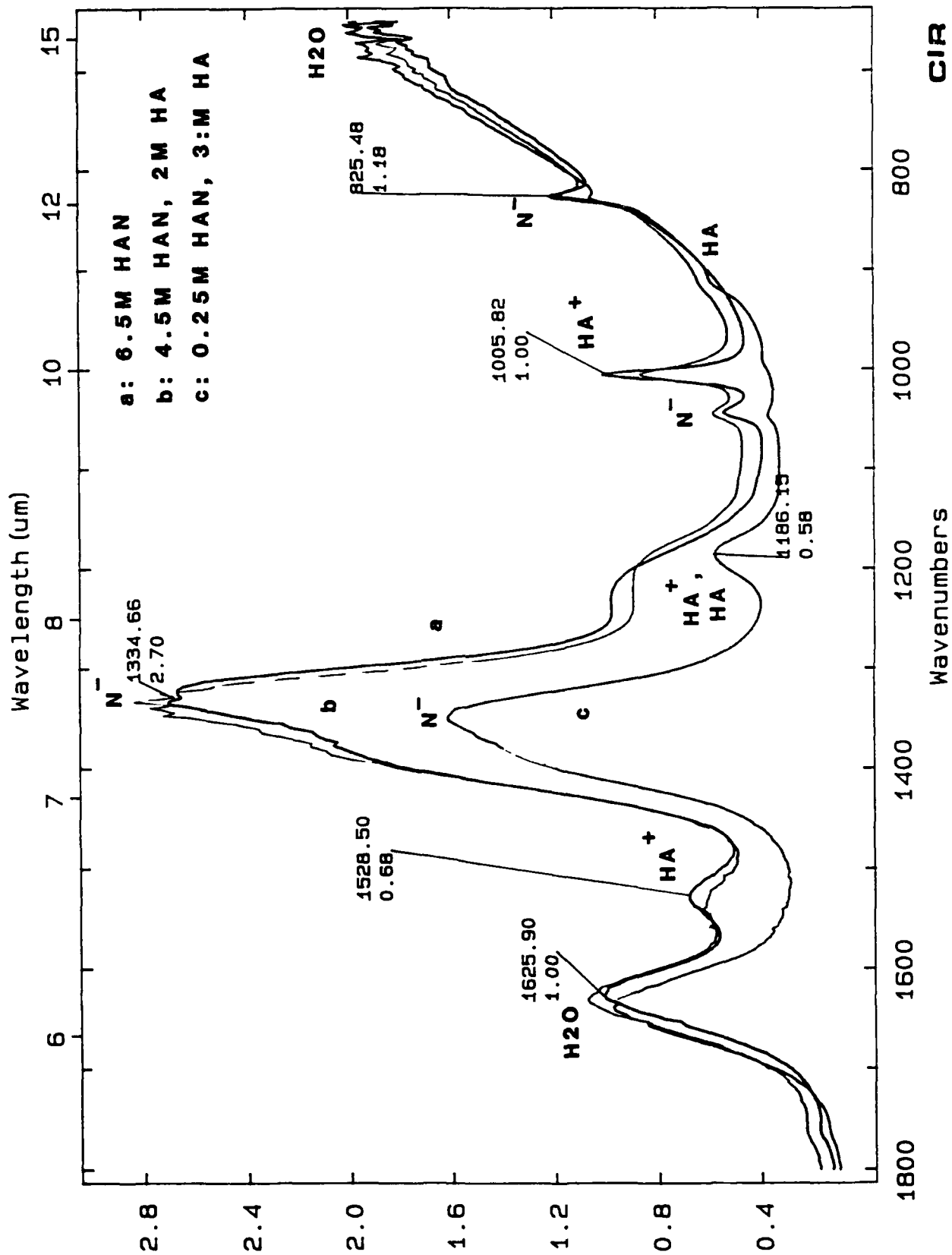
A b s o r b a n c e

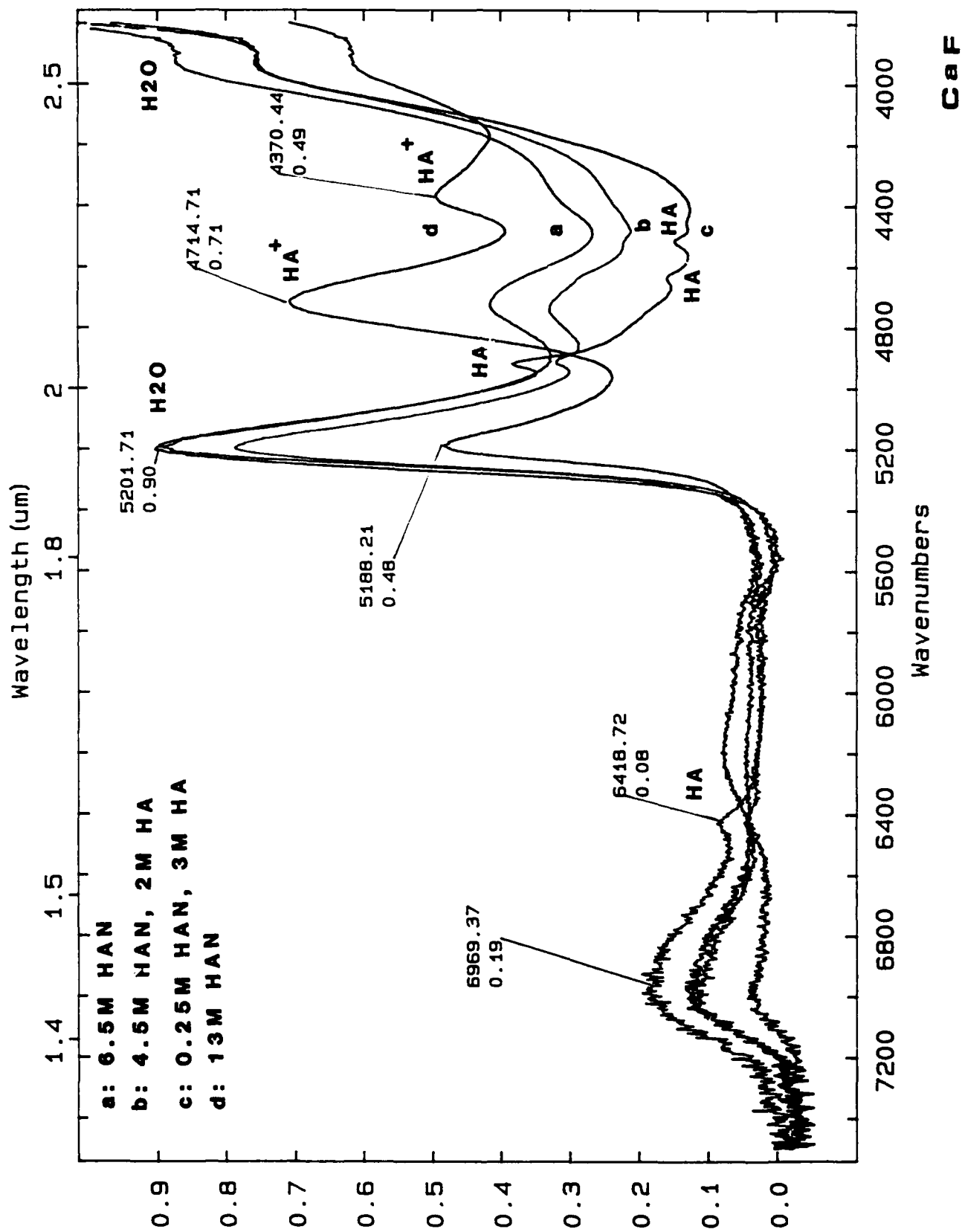


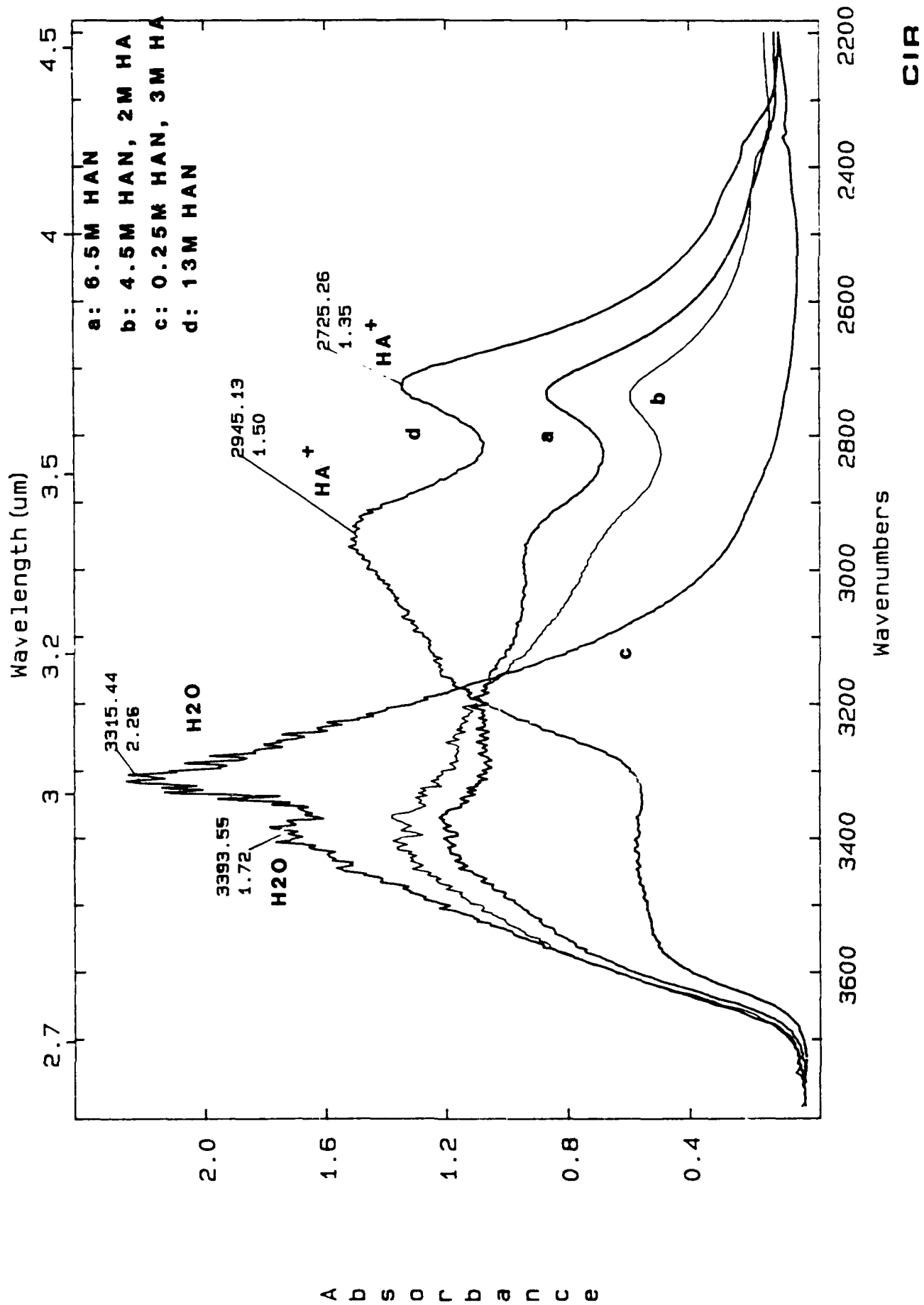


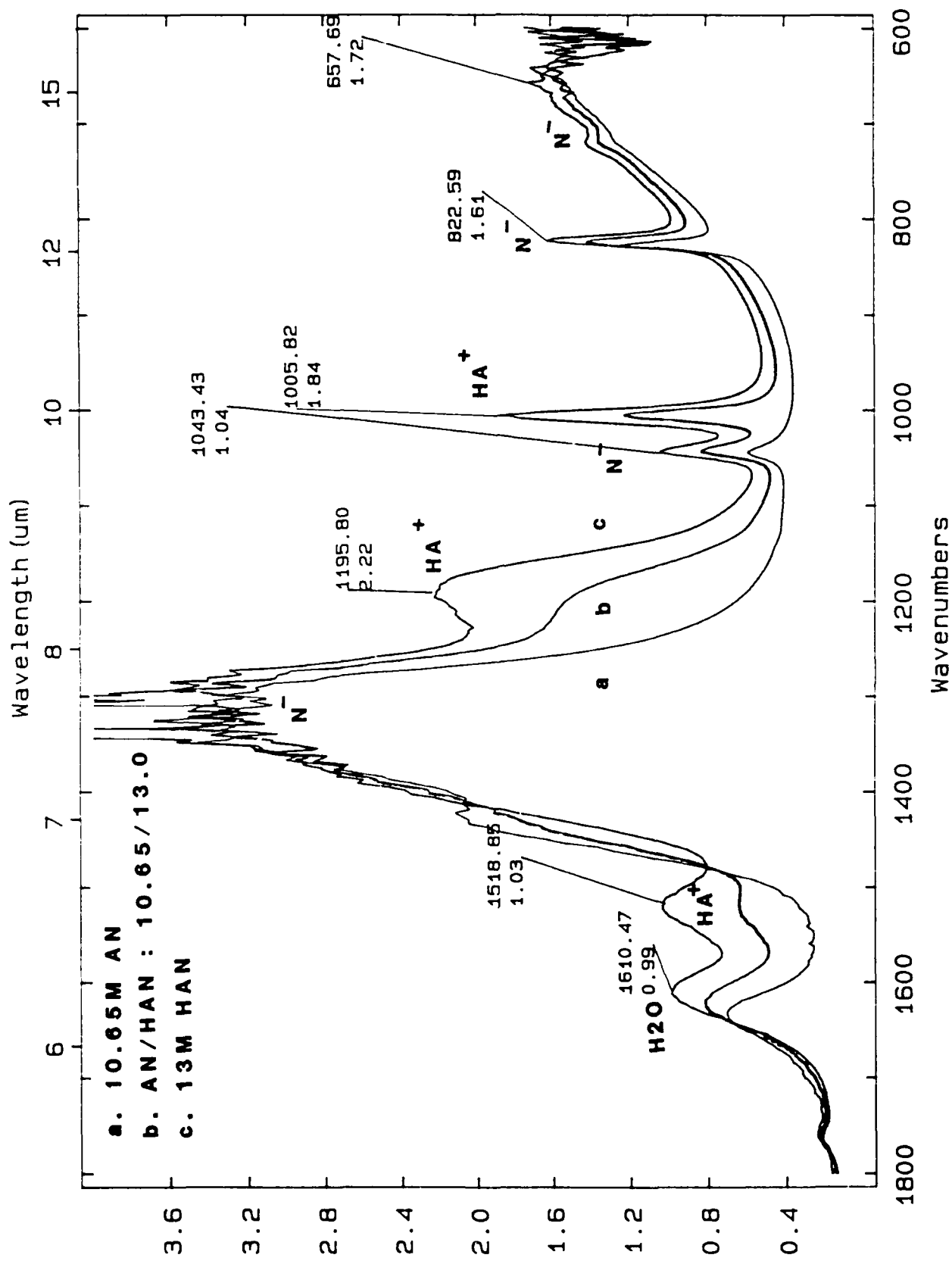












CIR

The Anomalous Behaviour of HAN-Based Liquid Gun  
Propellant During Analysis  
(Part 1, Isothermal Studies)

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Summary

This is the first of 2 papers in which a number of unexpected, non-reproducible events which have been observed when analysing HAN-based liquid gun propellant, are described.

A series of tests carried out isothermally at 77°C are reported. The occasional observation of rapid increases in reaction rate after a quiescent period of variable length, are noted. These events appear to be confined to propellants that have been subjected to accelerated ageing tests.

\* \* \*

***N.B. This document is intended to support a verbal presentation to be given at the 5th Annual Conference on HAN-Based Liquid Propellants, Structure and Properties, at the Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland. It reproduces some of the material reported in RARDE Memorandum 23/88, but includes some additional results that have been gathered since that Memorandum went to press.***

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## INTRODUCTION

Various methods for quantifying the stability of HAN-based liquid gun propellant have been developed at RARDE/WA and have been used to show the effect on thermal stability of contamination with metal ions [Ref 1,2].

Recently, a set of 5 samples of LPG was received from Royal Ordnance PLC, Westcott that had been subjected to a variety of material compatibility contact tests at elevated temperatures [Ref 3]. An estimate of any changes in thermal stability was requested.

These samples were subjected to the heat generation test described in Reference 1 and, in many cases, behaved in a manner that previous experience would suggest was consistent with the quantity of iron ions taken into solution (up to 10 ppm [Ref 4]), ie a slightly elevated, but constant heat generation rate. However, in a number of cases a sudden, unexpected, rapid increase in heat generation was observed, followed in some cases by a violent pressure burst of the sample ampoule.

A series of experiments was carried out to describe this phenomenon and to attempt to identify its cause.

## EXPERIMENTATION

### Equipment and Materials

All experiments using the bioactivity monitor were carried out with the experimental facility described previously [Ref 1].

All burst experiments were performed in an aluminum block maintained at a constant temperature of 77°C in a Grants block bath.

The trials at Westcott used LP101 blend 4 which had been manufactured at RO Waltham Abbey. The descriptions of the 5 samples supplied by RO Westcott were as follows:

- TUBE 1 316 SS welded transverse to rolling direction, 13 days at 69°C.
- TUBE 2 316 SS 2 specimens welded parallel to rolling direction, 15 days at 69°C
- TUBE 4 19.5.88 - 2.6.88 at 69°C in contact with polythene.
- TUBE 5 19.5.88 - 2.6.88 at 69°C in contact with polythene.
- TUBE 6 19.5.88 - 2.6.88 at 69°C in contact with polyvinylidifluoride.

A stock sample of LP101 blend 4 was used for control purposes.

The visual appearance of these samples varied from a pale yellow color, to a fairly deep orange. All were clear, homogeneous liquids.

#### Experimental Work. Results Observations and Remarks

This section will take the form of a descriptive account of some events that have been observed when using this group of propellant samples, in chronological order, along with some discussion of the reasons for proceeding with the next experiment.

##### Experiment 1

The variation of the heat generation rate with time of 2x4g samples from TUBE 1 and 2x4g samples from TUBE 2 when held at 77°C was monitored. These outputs settled down to reproducible, constant rates of 18  $\mu\text{W/g}$  and 20  $\mu\text{W/g}$  respectively. After about 6 h, one of the two samples from TUBE 2 showed an apparent sudden increase in heat generation rate which exceeded the range of the recording device. This had dropped back to a lower, constant rate by the time that this behaviour was noticed (Fig 1). The duplicate experiment, using material also taken from TUBE 2, showed no sign of this sort of behaviour and recorded a steady rate throughout the duration of the test (Fig 2). On removal of all 4 samples from the BAM the sample that had shown the apparent excursion had not burst, and showed no change in color or any sign of bubble formation, ie it was visually similar to its duplicate.

##### *Remarks Concerning Experiment 1*

*This anomalous behaviour had never been encountered before in the 18 months that the test had been in use, and it was felt at the time, that it could be due to a false signal being recorded caused by a malfunction in the amplifier. It was decided to continue with the analysis of samples from TUBES 4 and 5 and to observe the suspect amplifier carefully, to see if the problem reoccurred.*

##### Experiment 2

2x4g samples from TUBES 4 and 5 were subjected to the heat generation test. After about 2h it was noticed that one of the samples from TUBE 5 had suddenly gone offscale (ie apparently generating a large amount of heat). An attempt was made to remove it from the cylinder, but the ampoule was discovered to be detached from its lifting tool. The other three samples were showing no sign of high heat generation rates, but were removed from their cylinders to prevent

possible damage. Closer inspection of the unit that had given a high result revealed that the ampoule had burst, causing distortion of the BAM sample well.

#### ***Remarks Concerning Experiment 2***

*The cylinder containing the burst ampoule was not the same one that showed the transient peak during experiment 1. Thus this seems to be a real result of a change in the propellant itself and not some artificial detection fault. Because of the expense of replacing a damaged BAM cylinder, it was decided not to leave the BAM unattended with this material in it until the cause of these events had been found. It was thought possible that this sort of behaviour could be caused by the corrosive action of the contents of an ampoule leaking onto metal components within the detection region of the BAM and experiment 3 was proposed using the surviving 3 cylinders to see if this behaviour could be repeated.*

#### **Experiment 3**

3x4g samples of material from TUBE 5 were subjected to the heat generation test and kept under constant manual supervision to allow removal of the offending ampoule if a sudden exotherm was seen. After about 3/4 h one of the three outputs suddenly went offscale. This ampoule was removed from the cylinder immediately and a visual inspection showed no sign of leaks or a rapid reaction. It was then placed on the laboratory bench to cool down on the assumption that this would effectively halt any reaction that was still taking place. After 2-3 minutes this ampoule burst violently! Observation of the other 2 cylinders continued for a further 2 hours, but no anomalous behaviour was seen and the experiment was terminated.

#### ***Remarks Concerning Experiment 3***

*The increase in heat generation rate must have been enormous to continue the reaction rapidly enough to burst the ampoule while it was standing in the cool environment of the laboratory. The most notable feature of the observed effect was that, although the experiment succeeded in repeating the result seen in experiment 2, it could not be done reproducibly - ie bursting did not occur in all cases and, when it did occur, the same induction period was not seen prior to the event.*

#### **Experiment 4**

A 'time to pressure burst test' was performed on 2 samples from TUBE 5 at 118°C using the procedure outlined in Reference 2. Surprisingly, the time taken to record a burst was 17 h in both cases - a result consistent with the steady heat generation given by those samples from TUBE 5 which did



not burst - and these results would not have given any warning of instability at a temperature 41 degrees lower.

#### ***Remarks Concerning Experiment 4***

*The size of sample used in the TTPB test is slightly smaller than that employed for the HFC test, making accidental contamination of the cap by the ampoule contents less likely. Therefore one possible explanation for the odd behaviour seen in experiments 1, 2 and 3 advanced at this time was that accidental contamination of the cap by the propellant had allowed some violently incompatible material to come into contact with the propellant after a variable delay introduced by the time for diffusion to occur.*

#### **Experiment 5**

A larger number of heating trials were carried out in identical ampoules and using similar conditions to those used in the HFC test except that the ampoules were held in a robust heated aluminum block bath and the duration of the trial was 3 days. No attempt was made to determine the exact time that a burst occurred other than a visual inspection. The results of these trials are summarized in Table 1.

#### ***Remarks Concerning Experiment 5***

*It can be seen that bursts occurred sporadically in samples that had been subjected to accelerated ageing/contact trials and there was no significant difference between the frequency of burst and the type of material with which the propellant had been in contact.*

#### **Experiment 6**

20x4g samples of untreated LP101 propellant blend 4, which had been stored in a magazine since manufacture were also placed in a block bath at 77°C. In this case, no bursts occurred within 3 days.

#### ***Remarks Concerning Experiment 6***

*These negative results would suggest that this low temperature bursting behaviour was confined to samples received from RO Westcott.*

#### **Attempts To Duplicate the Original Observations**

At this stage, although it seemed that some treatment received by these samples during the time they were at Westcott, it was not clear whether this was due to the intended treatment (ie the desired compatibility trial) or some adventitious treatment (eg unintentional contamination

The following features should be emphasized.

- Considering both sets of results together it would appear that the anomalous behaviour was seen in the second group, although at a significantly reduced frequency in comparison to the first group.

To identify the cause of these events will require the use of more specific techniques than those employed for this study and a program of work to investigate this subject further is being prepared.

#### REFERENCES (cont.)

- 4 Moore M RO Westcott, Private Communication, 1988.  
5 Haworth J W RARDE Memorandum 18/89, 1989.

#### SYMBOLS AND ABBREVIATIONS

HAN	Hydroxylammonium nitrate
RO	Royal Ordnance
ppm	Parts per million (weight/weight)
HFC	Heat flow calorimeter
BAM	Bioactivity monitor
TTPB	Time to pressure burst
W	Watts
g	Grammes
h	Hours
LP101	A British copy of the US propellant LP1845

TABLE 1

## BLOCK BATH STORAGE TESTS

Sample no.	Wt (g)	Source	Final Appearance of Ampoule After 72 h
1	3.924	TUBE 2	no burst
2	4.125	TUBE 2	no burst
3	4.075	TUBE 2	no burst
4	3.929	TUBE 2	no burst
5	4.027	TUBE 2	burst
6	3.942	TUBE 2	no burst
7	3.931	TUBE 2	burst
8	4.030	TUBE 2	burst
9	3.918	TUBE 1	burst
10	3.938	TUBE 1	burst
11	3.936	TUBE 1	no burst
12	3.937	TUBE 1	burst
13	4.026	TUBE 1	burst
14	4.158	TUBE 1	burst
15	3.896	TUBE 1	no burst
16	3.932	TUBE 1	burst
17	3.987	TUBE 1	burst
18	4.015	TUBE 1	no burst
19	3.991	TUBE 6	no burst
20	3.899	TUBE 6	no burst
21	4.093	TUBE 6	no burst
22	3.978	TUBE 6	burst
23	3.982	TUBE 6	no burst
24	4.194	TUBE 6	burst
25	4.012	TUBE 6	no burst
26	3.901	TUBE 6	no burst
27	4.012	TUBE 6	no burst
28	4.019	TUBE 6	no burst

CONDITIONS: Approx. 4g samples of liquid propellant sealed in  
3 cm<sup>3</sup> glass ampoules with teflon-lined caps  
maintained at 77°C

SUMMARY: 12 burst seen out of a total of 28 trials

**TABLE 2      ATTEMPTS TO REPEAT THE ORIGINAL OBSERVATIONS**

i                      Summary of Pressure Burst Tests

	Sample/Contaminant	Burst Frequency
1	316 Stainless Steel	0 bursts from 10 trials
2	Solvirel Rubber Seal	2 bursts from 10 trials
3	Polythene DG/MPD/139B	1 burst from 10 trials
4	Polythene Stanylex 4036	0 bursts from 10 trials
5	Polyvinyl Difluoride	0 bursts from 10 trials
6	Aged Control*	2 bursts from 10 trials
7	Unaged Control!	0 bursts from 20 trials

\* ie Propellant that had been subjected to the trial conditions described in Reference 3, but with no solid test material in contact

! Stored in magazine at Waltham Abbey since manufacture

ii                      Summary of Heat Flow Calorimetry Tests

The highest constant rate of heat generation was given by the sample which had been in contact with 316 stainless steel (about 10-11  $\mu\text{W/g}$ ). All of the other samples showed very slightly elevated heat generation rates (6-7  $\mu\text{W/g}$  after 6 h). In no case was a sudden transition to rapid heat generation rate seen during the duration of these tests (6 h).

iii                      Visual Appearance of Second Set of Samples on Arrival at Waltham Abbey

All six samples received from Westcott were clear liquids colored a light straw color and were all of similar visual appearance. In this way they differed from the original set, which varied in color from light straw color to a fairly deep orange.

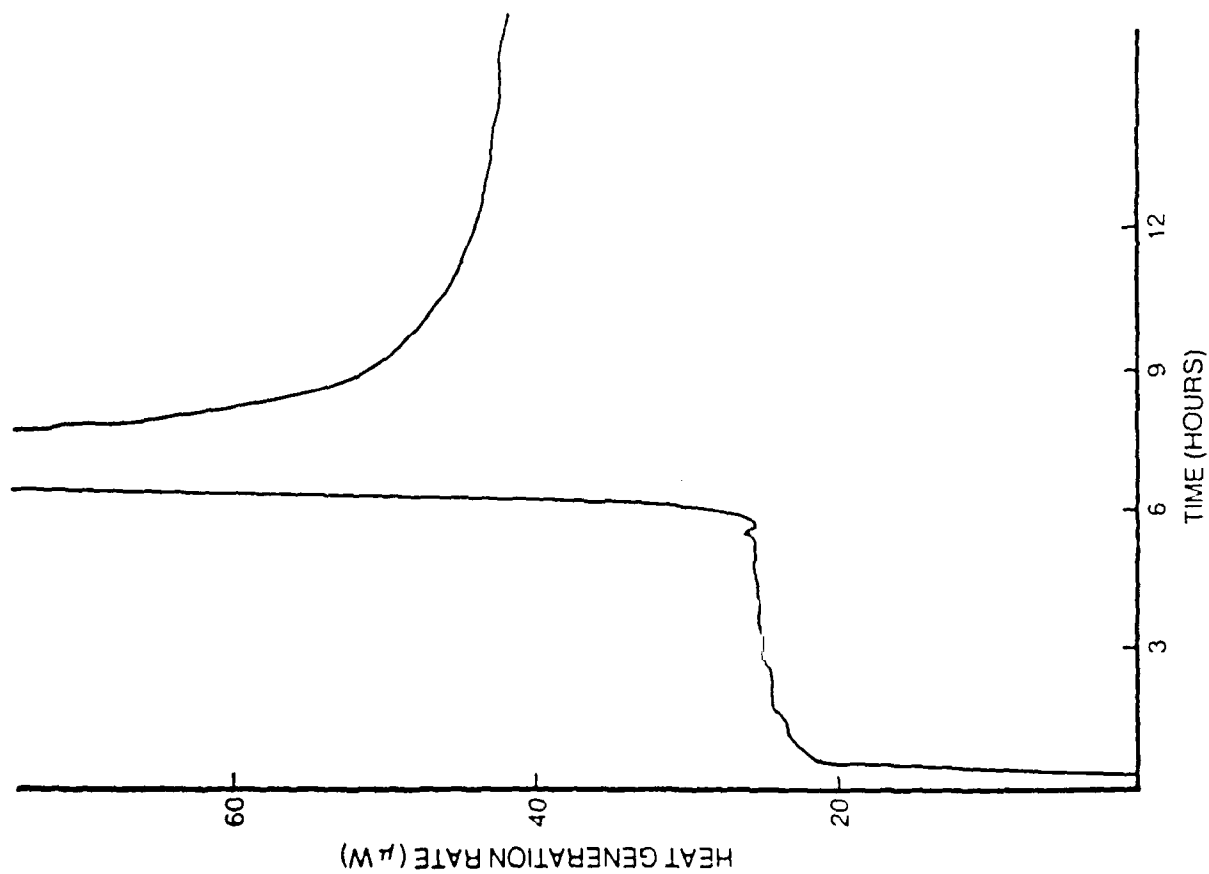


FIG. 1 4g LP101 FROM TUBE 2 - SHOWING "ANOMALOUS" BEHAVIOUR

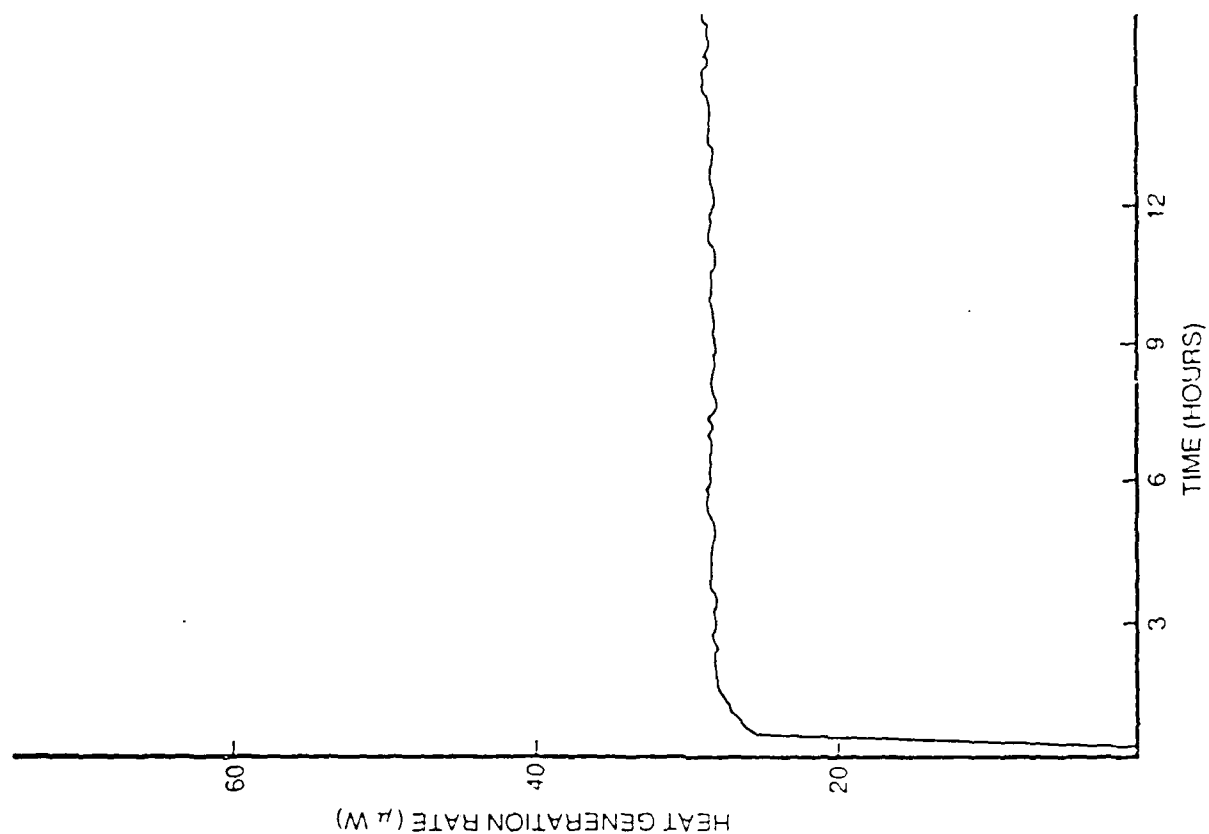


FIG. 2 4g LP101 FROM TUBE 2 - SHOWING "NORMAL" BEHAVIOUR

THE ANOMOLOUS BEHAVIOUR

OF HAN-BASED LIQUID

GUN PROPELLANT

P F BUNYAN  
S WESTLAKE

# PART 1

## ISOTHERMAL STUDIES



## COMPATIBILITY TEST

- 1) LP placed in reaction vessel fitted with pressure transducer.
- 2) Reaction vessel heated at 69°C for 14 days.
- 3) Gas evolution measured.
- 4) Sample placed in LP and test restarted & run for 14 days.
- 5) Sample removed. Test continued for further 14 days.

LP heated at 69°C for 6 weeks in total

## LP Samples Recieved

Had been in contact with :-

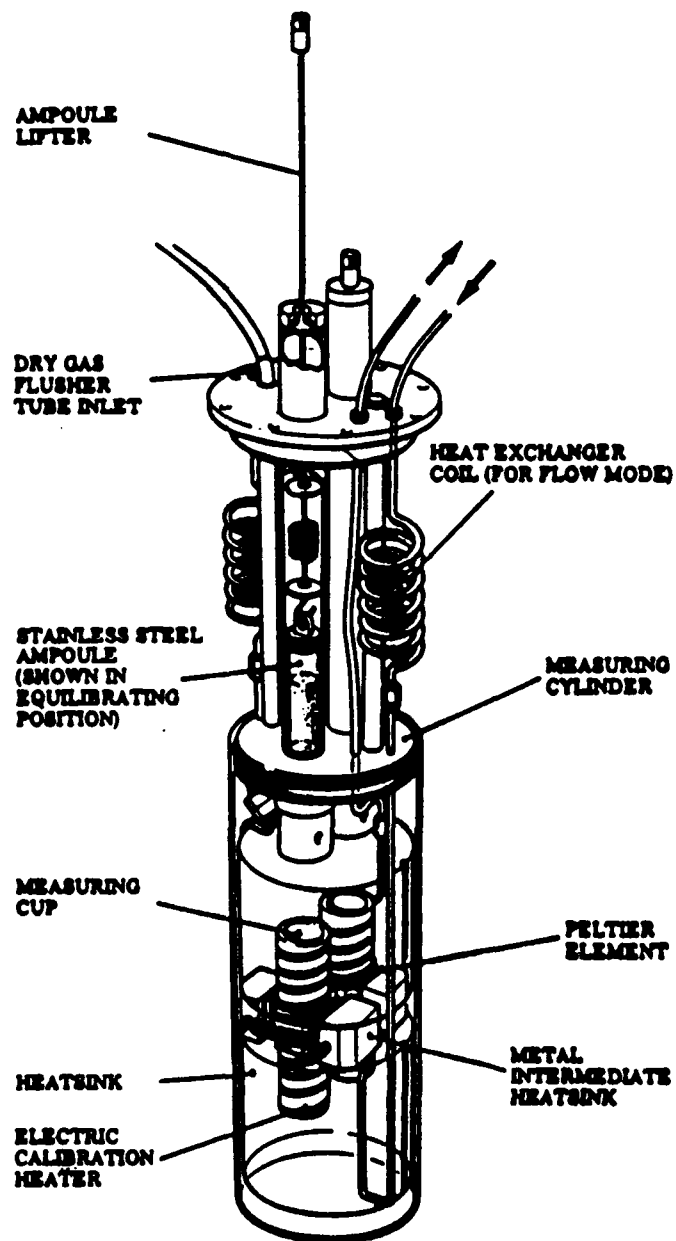
- 1) 316 SS transverse weld; contact time 13 days.
- 2) 316 SS parallel weld; contact time 15 days.
- 4) Polythene DG/MPD/139B black; contact time 14 days.
- 5) Polythene Stanylex; contact time 14 days.
- 6) 4036 Neutral PVDF sheet; contact time 14 days

## REQUEST

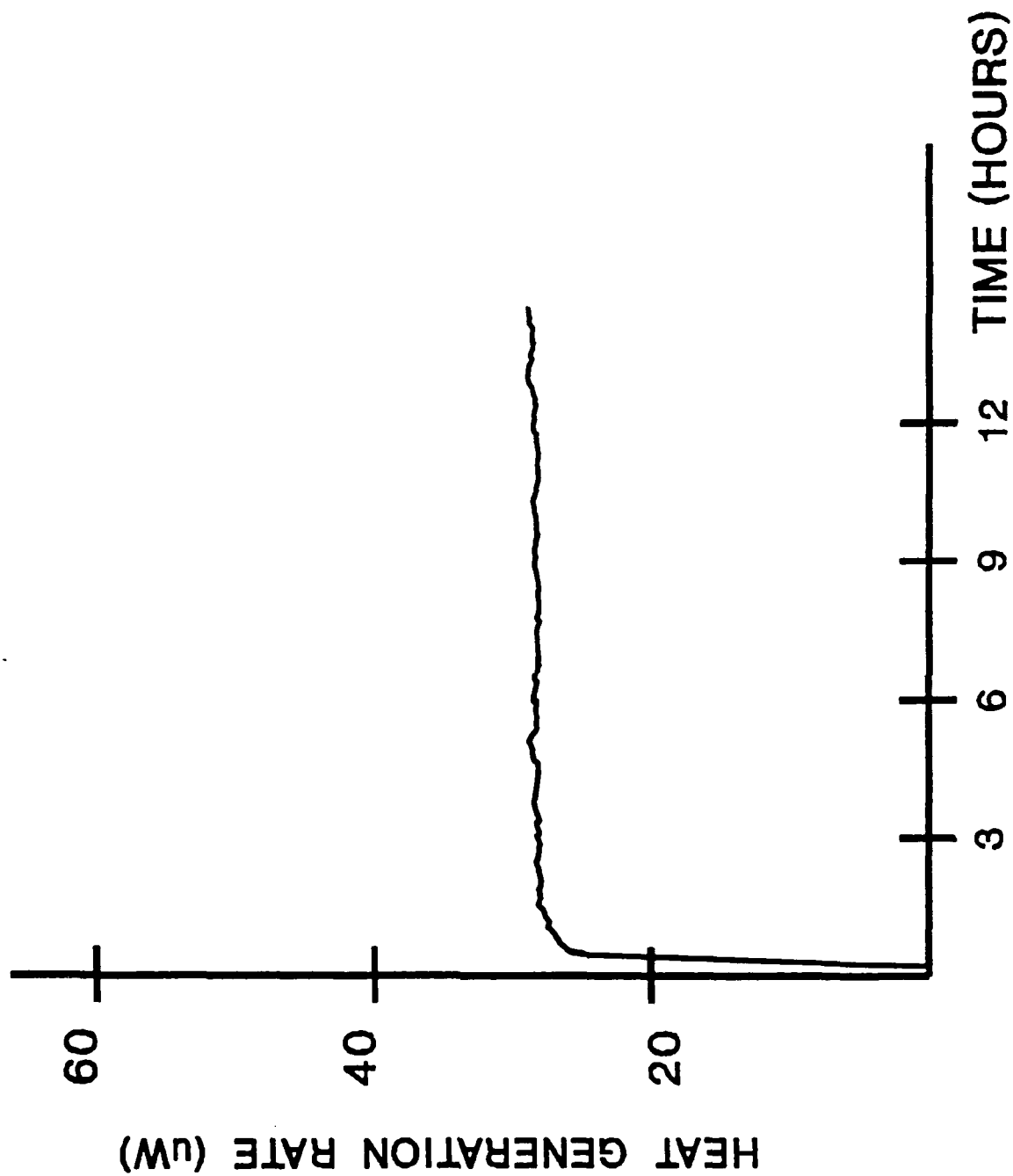
Establish if any changes in thermal stability had occurred.

## USED

The heat generation test.



## "Normal" Heat Generation Behaviour



# HEAT GENERATION TEST

## Exp 1-3

Temperature : 77°C

Test Duration : Variable

Sample Size : 4 g

Reaction Vessel : 3 cm<sup>3</sup> Sealed glass  
ampoule.

## RESULTS OF Exp. 1 & 2

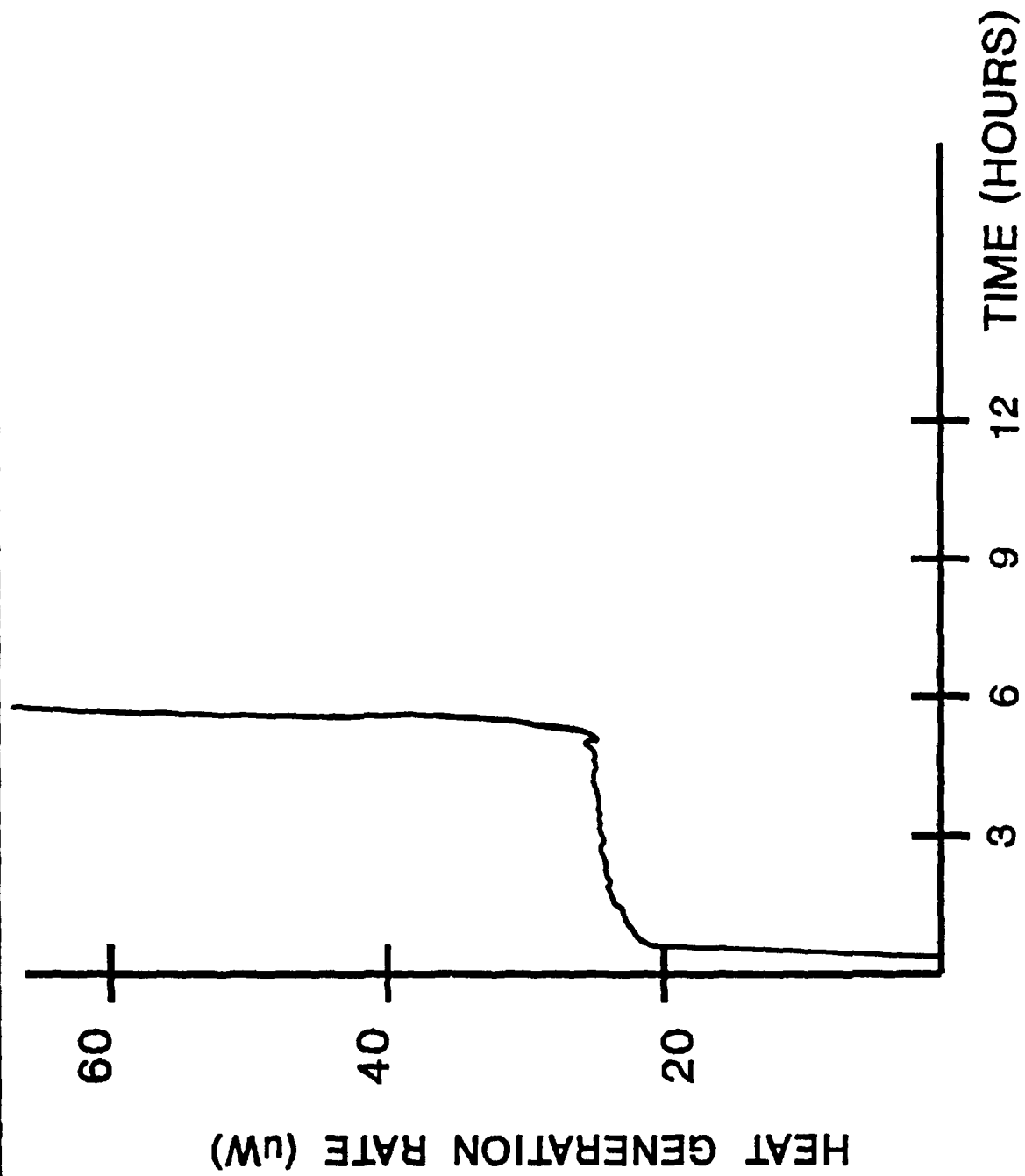
### Exp 1 : 4 tests on samples 1 & 2

- \* 3 tests behaved "Normally"
- \* 1 test (sample 2) showed a sudden increase in heat generation after 6 hrs.

### Exp 2 : 4 tests on samples 4 & 5

- \* 3 tests behaved "Normally"
- \* 1 test (sample 5) showed a sudden increase in heat generation after 2 hrs.
- \* Caused a pressure burst

# "ANOMALOUS" Heat Generation Behaviour





## RESULTS OF Exp. 3

### 3 tests on sample 5

- \* 2 tests behaved "Normally"
- \* 1 test showed a sudden increase in heat generation after 3 hrs.
- \* Sample removed and allowed to cool.
- \* 2 minutes later ampoule burst violently

## SUMMARY OF Exp. 1-3

- \* Sudden increase in heat generation observed
- \* Effect unpredictable
- \* Effect non-reproducible

# TIME to PRESSURE BURST TEST

## Exp 4

Temperature : 118°C

Test Duration : until pressure burst occurs

Sample Size : 3 g

Reaction Vessel : 3 cm<sup>3</sup> Sealed glass ampoule  
(seals burst between 6 & 8 atmos)

Sample : No. 5

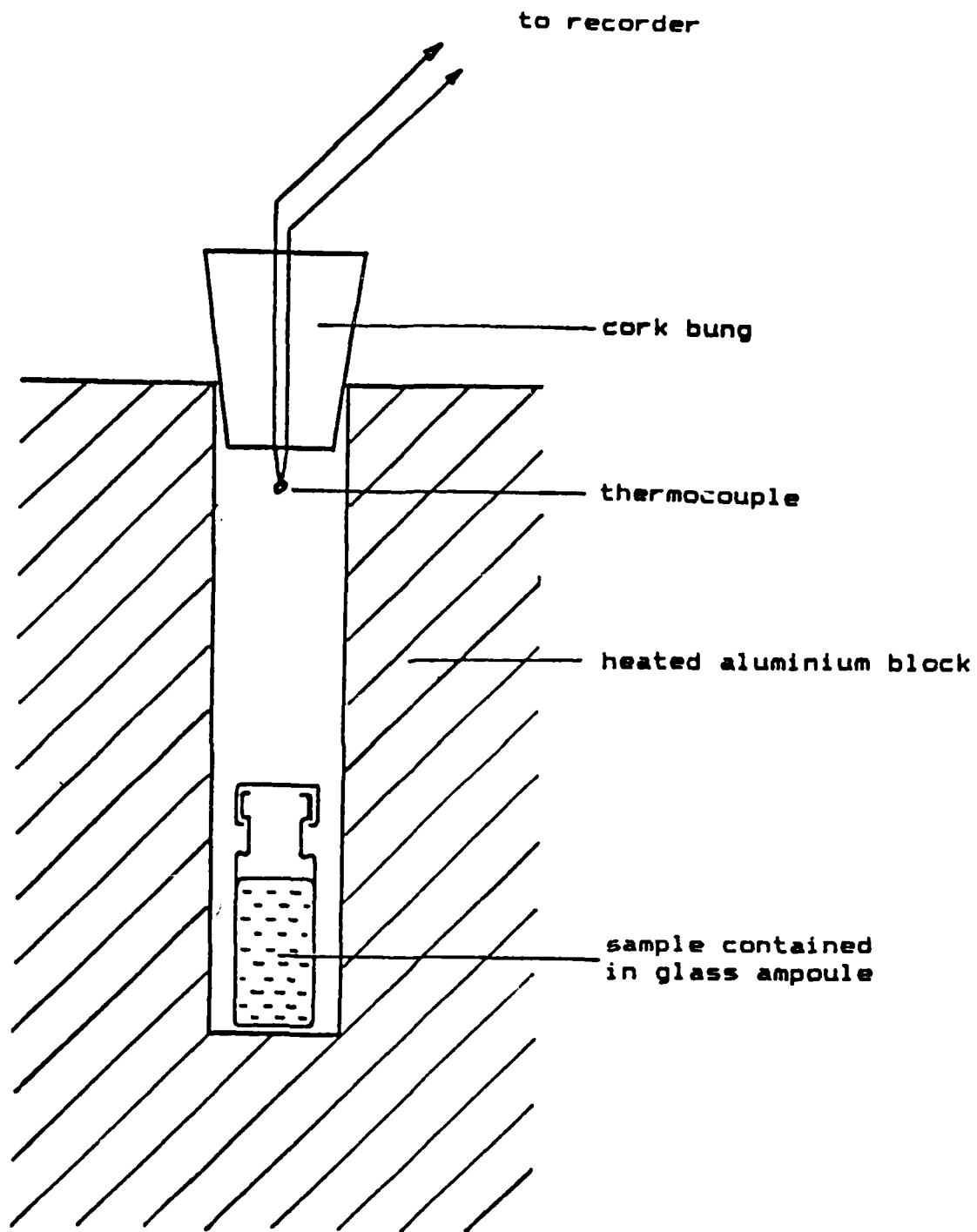


FIGURE 3

PRESSURE BURST TEST - SAMPLE CONFIGURATION

## RESULTS of Exp. 4

- \* Time to pressure burst : 17 hours
- \* Result consistent with the "Normal" steady  
Heat Generation given by samples from  
tube 5.

# BLOCK BATH TEST

## Exp 5&6

Temperature : 77°C

Test Duration : 3 days

Sample Size : 4 g

Reaction Vessel : 3 cm<sup>3</sup> Sealed glass  
ampoule.

Test Run : 8 - 10 samples

# RESULTS of Exp 5 & 6

Sample	No. of Bursts	No. of Tests
2	3	8
1	7	10
6	2	10
untreated LP101	0	20

## 77° C BLOCK BATH STORAGE TESTS

### - PRINCIPAL OBSERVATIONS

- 1) Bursts occurred sporadically
- 2) No difference due to type of solid material in contact.
- 3) Bursts only seen in the case of propellant obtained from heating trials.
- 4) Surviving ampoules showed no sign of being about to burst.



## ARE OBSERVED EVENTS DUE TO :-

### Compatibility Test

- Contact with foreign material
- Heating programme

### Contamination During :-

- Storage
- Transportation
- Thermal stability tests.

# RESULTS of REPEAT TRIALS

## BLOCK BATH TEST

<u>Sample/Contaminant</u>	<u>No. of Bursts</u>	<u>No. of Tests</u>
1) 316 SS	0	10
2) Solvirel Rubber Seal	2	10
3) Polythene DG/MPD/139B	1	10
4) Polythene Stanylex 4036	0	10
5) PVDF	0	10
6) Aged Control	2	10
7) Unaged Control	0	20

## OBSERVATIONS WHEN ANALYSING MATERIAL FROM REPEATED STORAGE TRIAL

- 1) No anomalous events observed in HFC.
- 2) Some bursts seen in the block bath tests, but less frequently than from earlier samples.
- 3) As before, there was no connection between frequency of bursts & the type of foreign material.
- 4) As before, surviving ampoules showed no sign of being about to burst.

# COMPARISON BETWEEN FIRST & SECOND SET OF PROPELLANTS RECEIVED FROM WESTCOTT

**Original set : 12 bursts seen out of 36 trials**

**Repeated set : 5 bursts seen out of 60 trials**

**Unheated propellant : no bursts out of 40 trials**

**No difference to burst behaviour appears to be  
caused by the type of solid material used in  
the contact test.**

**PAULS**

# EXTENDED BLOCK BATH TEST

Sample : Stock LP101

Test Duration : 22 days

No. of test samples : 20

Test Temperature : 77°C

Results : 10 bursts within 22 days
------------------------------------

**The Anomalous Behaviour of HAN-Based Liquid Gun  
Propellant During Analysis  
(Part 2, Adiabatic Studies)**

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**Summary**

This is the second of 2 papers in which a number of unexpected, non-reproducible events which have been observed when analysing HAN-based liquid gun propellant, are described.

Some results obtained on this propellant using an adiabatic calorimeter are presented. Variable results and a sudden transition from slow to rapid reaction rate again appear to be characteristics of this propellant. In this case, the propellant employed for the experiments was unaged.

\* \* \*

***N.B. This document is intended to support a verbal presentation to be given at the 5th Annual Conference on HAN-Based Liquid Propellants, Structure and Properties, at the Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland. It reproduces some of the material reported in RARDE Memorandum 9/89, but includes some additional results that have been gathered since that Memorandum went to press.***

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## INTRODUCTION

The suggestion was made at the end of the 4th Annual Conference on HAN-based Propellants that the theory of thermal explosions should be applied to this class of propellant in order to estimate its response to various situations when stored or transported in bulk (Ref 1).

The technique of adiabatic calorimetry has been used to gather data on the self heating behaviour of several energetic materials (Refs 2,3) and this can yield information concerning critical conditions for thermal runaway. An adiabatic calorimeter has recently been acquired by RARDE and, as part of an initial assessment of this technique, attempts have been made to obtain thermal runaway curves from samples of a HAN-based propellant under a variety of conditions.

The results obtained for HAN-based propellant were far more variable than seen with other energetic materials and it is difficult to see how any ordinary temperature/concentration dependent rate law could explain this. It appears that the application of the technique to this propellant will not yield data that can be interpreted using conventional thermal explosion theory.

These results bear features which resemble some of the observations reported in another paper at this conference and it appears likely that the sudden increases in heat generation rate seen during both isothermal and adiabatic studies are related.

## PROBLEM DEFINITION AND GENERAL APPROACHES TO A SOLUTION

Most<sup>1</sup> energetic materials have a large, positive, exponential dependence of decomposition rate on temperature. The rate of heat loss of a container has an approximately linear dependence on temperature. The practical consequence of these two facts is that any system containing a substance capable of self-heating can behave in one of two very different ways. Either the system will approach a steady state where heat generation and loss rate are equal or, if the sample mass is too large, initial temperature of the system too high, or the heat loss processes too slow, thermal runaway can occur leading to a thermal and/or pressure explosion.

<sup>1</sup> It is, of course, essential that the reaction which will be responsible for any potential explosion is one whose rapid decomposition mechanism is that of a thermal explosion for thermal explosion theory to be applied successfully to it.

Hazard evaluation for any material which, for example, didn't obey a positive dependence of rate on temperature type of law, would not be amenable to this sort of approach.

It is necessary to have some means of estimating the likely response of any system that contains energetic materials in bulk, to a variety of situations that they might encounter during their service life, so that remedial action can be taken to prevent an explosion, or at least predicted so that measures can be taken to minimize the resulting damage. In order to do this the following two questions must be addressed.

i To what temperature, in a given environment, can a particular system be raised and still be expected to cool again by itself? (ie what is its *critical temperature of no return*?)

ii If the system is heated to a temperature higher than that described in i, how much time is available before it explodes for remedial action to be taken such as hosing down with cold water or evacuating the area? (ie what is the *time to maximum rate*?)

If a valid, general model can be found which describes the self-heating behaviour of the system, then it could be applied to a larger scale system to provide answers to these questions. In order to do this it is necessary to quantify:

a The heat loss characteristics of the container. These can be calculated if the surface area, surface heat transfer coefficient and thermal capacity of the system are known. Alternatively, it can be measured experimentally by filling a similar container with a material of known specific heat and recording its cooling curve while the temperature of the surroundings is held constant.

b The laws governing the self-heating behaviour temperature and time caused by exothermic decomposition of the energetic material.

With this information, it is possible to construct an adiabatic time-temperature runaway curve and a heat loss rate curve on the same pair of axes. Critical conditions can be deduced from this plot by applying the theory of thermal explosions. A comprehensive description of thermal explosion theory may be found in reference 4.

If the energetic material of interest can be maintained under true adiabatic conditions while its temperature is monitored as a function of time, it may possible to obtain the runaway curve directly as an experimental result. An adiabatic calorimeter is manufactured by Columbia Scientific Industries, of Austin, Texas, USA, which subjects a sample to an adiabatic environment by surrounding it with electric heaters. Power supplied to the heaters is controlled by means of a feedback loop from a thermocouple in good thermal contact with the sample container and heat loss or gain prevented by ensuring that no temperature gradient develops between the sample and its immediate surroundings. The operating principles and theoretical aspects of data handling



of this device are described in References 5 and 6.

## EXPERIMENTATION

### Equipment and Materials

All experiments were performed using an accelerating rate calorimeter manufactured by Columbia Scientific Industries, Austin, Texas. The instrument was assembled, calibrated and operated following the procedures described in Reference 7.

Energetic materials were obtained from existing stock samples held by RARDE and were used without further purification.

Standard spherical titanium bombs and wide mouth hastelloy C bombs were supplied by CSI. Spherical tantalum bombs were obtained from The Ballistics Research Laboratory, Aberdeen, Maryland.

When wide-mouthed bombs were used, they were lined with glass by inserting an 18 mm dia. Samco flat bottomed tube cut down to a length of 19 mm.

Metal sample bombs were cleaned before use by heating to 600°C in an oven while purging the inside of the bomb with oxygen, to remove carbonaceous deposits.

### Experimental Work

Many of the experimental results reported here appeared originally in Reference 8, which was designed to assess the potential of the ARC to tackle a variety of problems of interest to RARDE. A range of energetic materials were therefore investigated for that study: Di-t-butyl peroxide, Iso-propyl nitrate, Liquid gun propellant LP101, Octofuel II and 1,3,5-trinitro-triazine (RDX). This paper, which is intended to highlight some unusual features of HAN-based gun propellant behaviour, will only describe ARC runs performed on LP101 and, for comparison, iso-propyl nitrate. However, it should be noted that many of the general features of the IPN trace are common to all of the other materials considered in the earlier document.

Data were processed, plotted and interpreted employing the theoretical principles and equations derived by Townsend and Tou (Ref 5).

Values for the specific heat of energetic materials, used for the calculation of  $\phi$  factor, were as reported in Reference 9.

A description of operating conditions and a summary of the result of each experiment are given in Table 1. As many of the individual ARC runs showed unique features, they are discussed in greater detail in the next section.

## Results and Observations - Individual Experiments

### LIQUID GUN PROPELLANT LP101

#### RUNS 1 2 AND 3

These runs were performed on untreated LP101 in standard spherical titanium bombs.

Run number 2 gave only one data point as an effectively instantaneous temperature jump occurred from 101 to 183 °C and no plot of this data has been attempted. Plots of temperature vs time for runs 1 and 3 are shown in Figs 1-2.

#### RUNS 4 AND 5

These runs were performed on LP101 which had been diluted down to about 20% solids with water in order to see if this would allow the reaction to take place in a slow, controlled manner, both by diluting the reactants, and by acting as a large heat sink in intimate contact with the reactants. Plots of temperature vs time are shown in Figs 3-4.

It can be seen that this was unsuccessful, the sudden, non-reproducible rate increases being seen in both cases. The temperature at which this occurs seems to be at a higher temperature than seen in the case of undiluted LP101 and to an extent that cannot be explained by increased thermal inertia ( $\phi$  factor) effects alone. It would appear that water may play a more important role in the reaction mechanism than that of a mere inert diluent.

#### RUNS 6 AND 7

This propellant has been shown to be very incompatible with many transition metals (Ref 10) and it was felt possible that the sharp changes in rate seen when using LP101 in the ARC could be an experimental artifact introduced by a reaction between the propellant and the bomb construction material (titanium).

Non-reproducible results have been reported in the past when this class of propellant has been analysed in ANSI 316 stainless steel bombs in the ARC (Ref 11) and the variability in results was ascribed to corrosion caused by incompatibility between the bomb and propellant in the vicinity where the alloy was welded. It was reported, in the same article, that tantalum bombs are now employed for ARC work on this material.

Runs 6 and 7 were therefore virtual repeats of run 2 and 3 except that tantalum bombs were employed in order to see if a more sedate decomposition could be achieved.

Run 6 gave only one data point since an effectively instantaneous temperature jump occurred from 98 to 133°C. Run

7 began to self-heat at 105°C and showed a slow, steady temperature increase up to 123°C, after which an effectively instantaneous reaction was seen (Fig 5). The behaviour of these two samples seems to fall within the wide range found before when using titanium bombs. The view that these two types of bomb were equivalent, as regards reactivity towards this propellant was supported by performing a semi-quantitative compatibility test using the heat flow calorimetry facility described in Reference 12. A small piece of 1/8" tube cut from the neck of a titanium bomb exhibited a low heat generation rate at 77°C, comparable to that shown by a similar piece of tantalum. Pieces of hastelloy C and 316 stainless steel bombs showed elevated rates in comparison, and a piece of copper pipe, which is known to be highly incompatible with LP101, showed an enormous heat generation rate. Results and conditions for these tests may be found in Figure 12.

#### RUNS 7-14

These runs were performed in wide-mouthed hastelloy C bombs which had been lined with a glass tube. This arrangement was used in order to see if contact of the propellant with any metal surface (even an apparently compatible one) were responsible for the sudden, non-reproducible transitions to rapid rate seen in the preceding experiments.

Temperature-time curves for runs 7 and 8 are shown in Figs 6 and 7 and it can be seen that slow self-heating was observed for several degrees before an explosive reaction was seen. In contrast runs 9 and 10 both appear to have suffered an explosive reaction without any prior self-heating. Although these results are similar to those seen with the spherical metal bombs as far as variability goes, the observed events all occurred at higher temperatures.

Although the relatively poor heat transmission through the glass liner and the very large  $\phi$  factor due to the mass of these bombs meant that these runs could only be considered semi-quantitative, these results would suggest that contact with metal surfaces might increase the likelihood of a rapid reaction occurring at a lower temperature.

This conjecture was tested by running samples of LP101 in similar glass lined hastelloy C bombs, but with small pieces of either tantalum or titanium immersed in the propellant. It can be seen that, although still variable, the temperature at which explosive events were observed were within the lower range seen before with the all-metal bombs (Table 1).

#### ISO-PROPYL NITRATE

#### RUNS 15 AND 16

Temperature-time curves for these runs are shown in Figures 8 and 9. It can be seen that, in contrast to the results

found with LP101, these runs duplicate well and a single, smooth decomposition curve is seen with no explosive reaction.

#### RUNS 17 AND 18

These runs were performed on small samples of IPN run in the glass-lined, open mouthed bombs in order to check that the presence of the glass liner did not act as a sufficiently good insulator to prevent the moderating influence of the bomb's thermal mass preventing a normal thermal explosion.

It can be seen that the exotherm was reproducible and no explosive event was observed. Self-heating was detected about 10° higher than seen when IPN was run in low-thermal-mass spherical titanium bombs. These results are consistent with the behaviour expected from a material displaying a temperature/concentration dependent general rate law, when an allowance is made for the large differences in  $\phi$  between the types of bomb used.

#### DISCUSSION

Taking the LP101 results as a whole, the most obvious feature is that the temperature of onset, the extent of reaction before a transition to explosion is seen and the shape of the continuous part of the curve are non-reproducible in comparison with 'well behaved' energetic materials. In fact the only persistent feature appears to be that a transition to very rapid rate always occurs at some point during the analysis. It is hard to see how any temperature/time dependent general rate law could fit these observations and it would appear that thermal explosion theory cannot be applied to these particular results. In this way, these results resemble those obtained from some LP101 samples during isothermal experiments and described as "anomalous behaviour" (Refs 13,14), and the causes of both sets of observations may be related.

Although conventional thermal explosion theory cannot be applied to these results, the ARC does provide a robust, controlled, instrumented containment vessel for following the entire decomposition of this material and it is hoped to use the device at RARDE to identify the factors which contribute to this phenomenon. In order to describe the detailed mechanism responsible for these observations further, it will be necessary to use a more specific analytical technique than calorimetry. To this end, a program of work, employing the technique of electron spin resonance spectroscopy to look for free radical species during HAN decomposition, is currently under consideration.

#### ACKNOWLEDGEMENT

The authors wish to thank Dr N Klein of the Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland, for

providing a set of tantalum sample bombs as a gift.

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#### SYMBOLS AND ABBREVIATIONS

HAN Hydroxylammonium nitrate  
IPN Iso-propyl nitrate  
ARC Accelerating rate calorimeter  
LP101 A British copy of the US propellant LP1845

TABLE 1

## ARC RUN DATA

Run No.	Sample	Bomb Type	Thermal Inertia ( $\phi$ )	Temperature At Which Self-Heating First Detected ( $^{\circ}\text{C}$ )
1	0.3544g LP101	Titanium	7.14	93 <sup>a</sup>
2	0.1847g LP101	Titanium	4.48	132 <sup>a</sup>
3	0.1604g LP101	Titanium	5.25	101 <sup>b</sup>
4	1.4191g LP101 <sup>c</sup>	Titanium	11.9	162 <sup>a</sup>
5	1.814g LP101 <sup>c</sup>	Titanium	8.7	183 <sup>a</sup>
6	0.1276g LP101	Tantalum	4.81	98.5 <sup>b</sup>
7	0.1302g LP101	Tantalum	5.05	105 <sup>a</sup>
8	0.4898g LP101	Hastelloy C <sup>d</sup>	23.2	129.8 <sup>a</sup>
9	0.4709g LP101	Hastelloy C <sup>d</sup>	24.1	132.6 <sup>a</sup>
10	0.4864g LP101	Hastelloy C <sup>d</sup>	23.4	134.9 <sup>b</sup>
11	0.3577g LP101	Hastelloy C <sup>d</sup>	31.0	123.8 <sup>b</sup>
12	0.2300g LP101 <sup>e</sup>	Hastelloy C <sup>d</sup>	48.3	106.2 <sup>b</sup>
13	0.1868g LP101 <sup>e</sup>	Hastelloy C <sup>d</sup>	58.4	107.0 <sup>b</sup>
14	0.1618g LP101 <sup>f</sup>	Hastelloy C <sup>d</sup>	67.3	113.0 <sup>b</sup>
15	0.1766g LP101 <sup>f</sup>	Hastelloy C <sup>d</sup>	61.8	95.0 <sup>b</sup>
16	0.1025g IPN	Titanium	5.72	149 <sup>g</sup>
17	0.1297g IPN	Titanium	5.65	146 <sup>g</sup>
18	0.1251g IPN	Hastelloy C <sup>d</sup>	104.9	159.5 <sup>g</sup>
19	0.1314g IPN	Hastelloy C <sup>d</sup>	98.6	159.7 <sup>g</sup>

<sup>a</sup> Initial slow, controlled self-heating followed by a sharp transition to rapid rate.

<sup>b</sup> Effectively instantaneous jump to final temperature as soon as self heating is detected.

<sup>c</sup> 26-28% wt/wt LP101 in water.

<sup>d</sup> Wide-mouthed bomb lined with an 18x19 mm glass tube.

<sup>e</sup> 2 pieces of 1/8" tantalum tube (0.264g) immersed in propellant.

<sup>f</sup> 2 pieces of 1/8" titanium tube (0.0691g) immersed in propellant.

<sup>g</sup> Uniform, controlled decomposition throughout recorded exotherm.

TEMPERATURE vs TIME PLOT

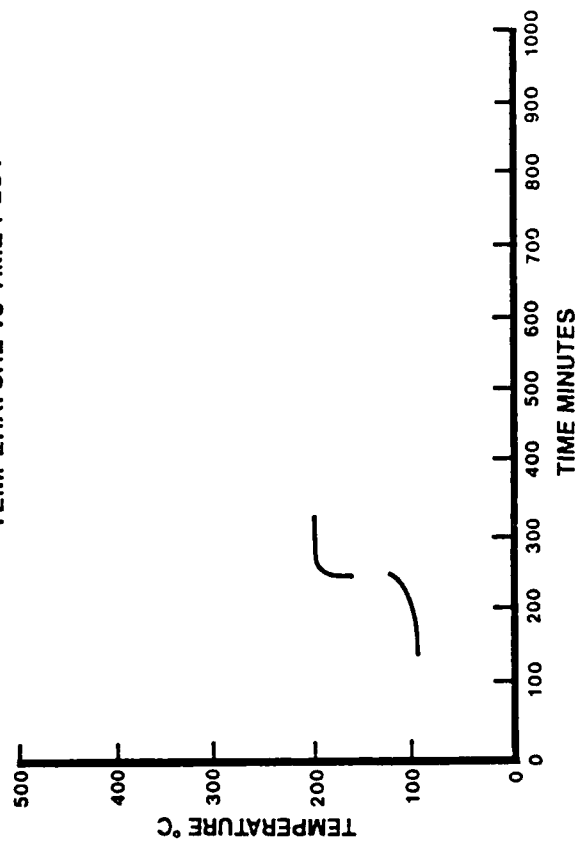


FIG 1 LP101 IN SPHERICAL TITANIUM BOMB

TEMPERATURE vs TIME PLOT

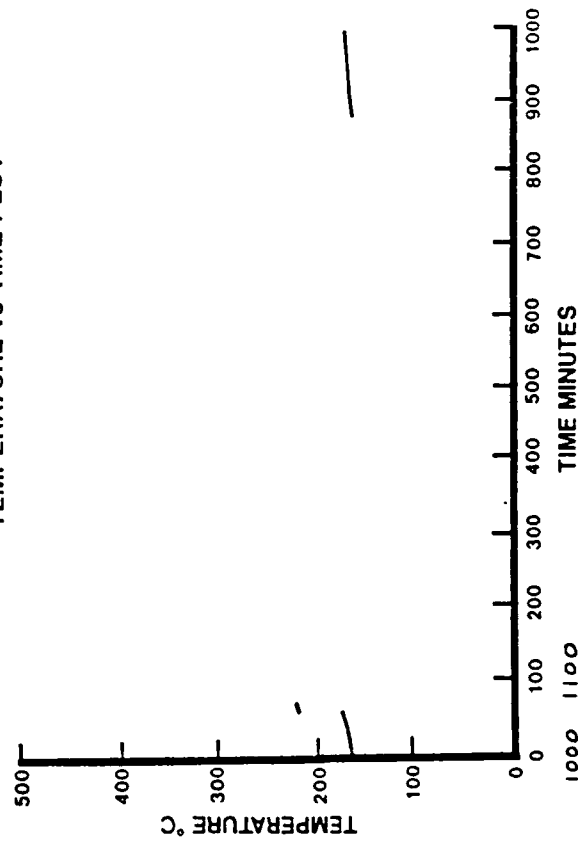


FIG 3 LP101 (DILUTED WITH WATER) IN SPHERICAL TITANIUM BOMB

TEMPERATURE vs TIME PLOT

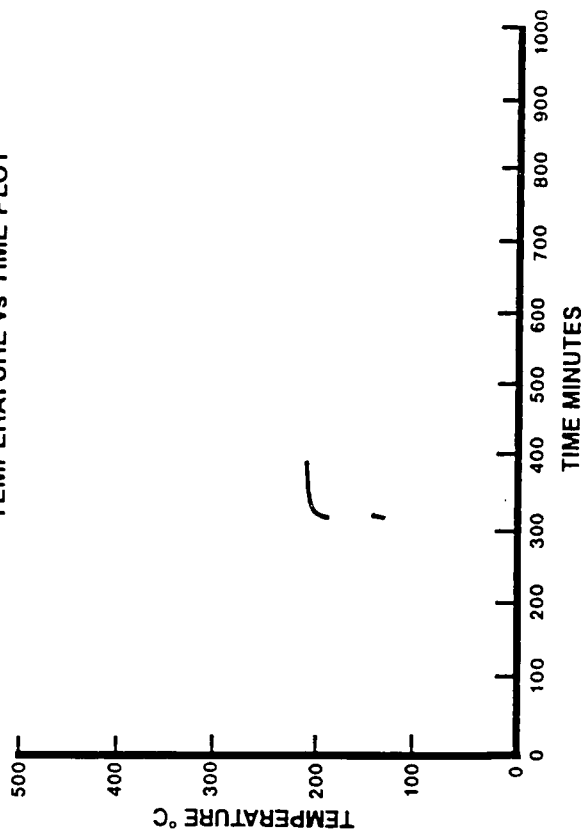


FIG 2 LP101 IN SPHERICAL TITANIUM BOMB

TEMPERATURE vs TIME PLOT

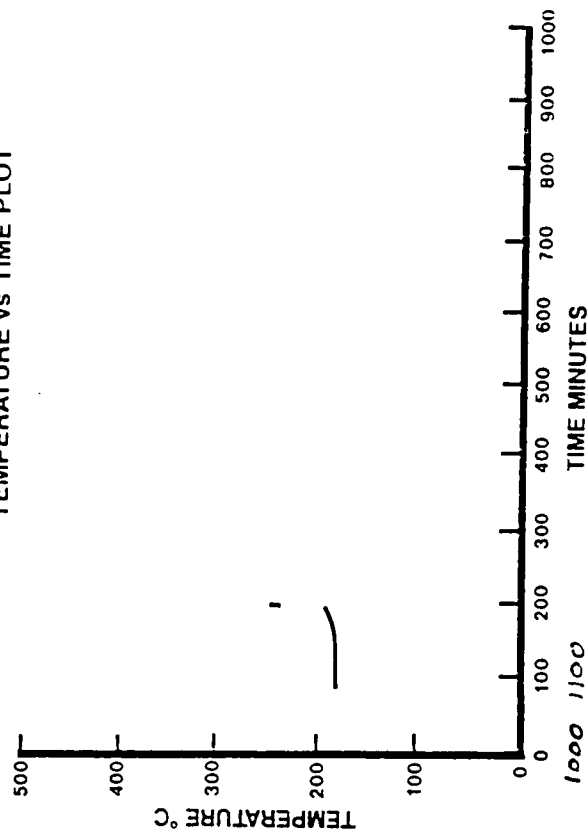


FIG 4 LP101 (DILUTED WITH WATER) IN SPHERICAL TITANIUM BOMB

TEMPERATURE vs TIME PLOT

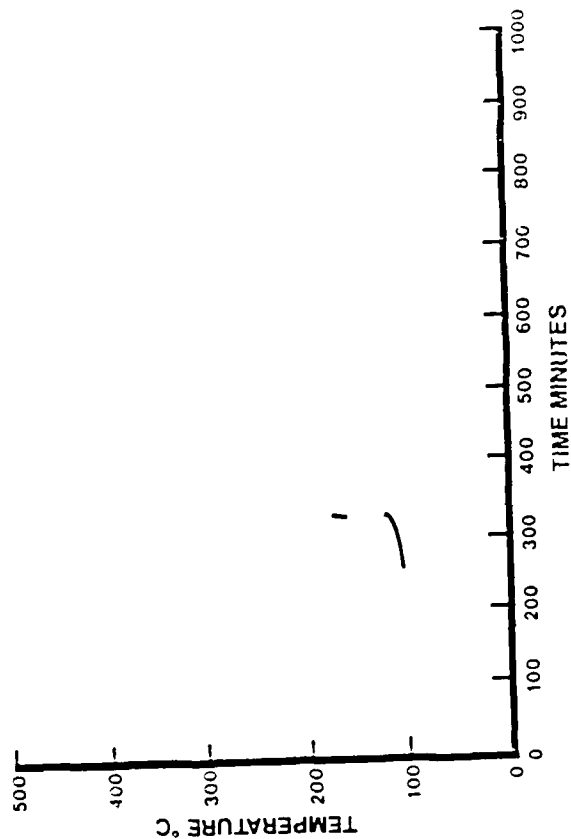


FIG 5 LP101 IN SPHERICAL TANTALUM BOMB

TEMPERATURE vs TIME PLOT

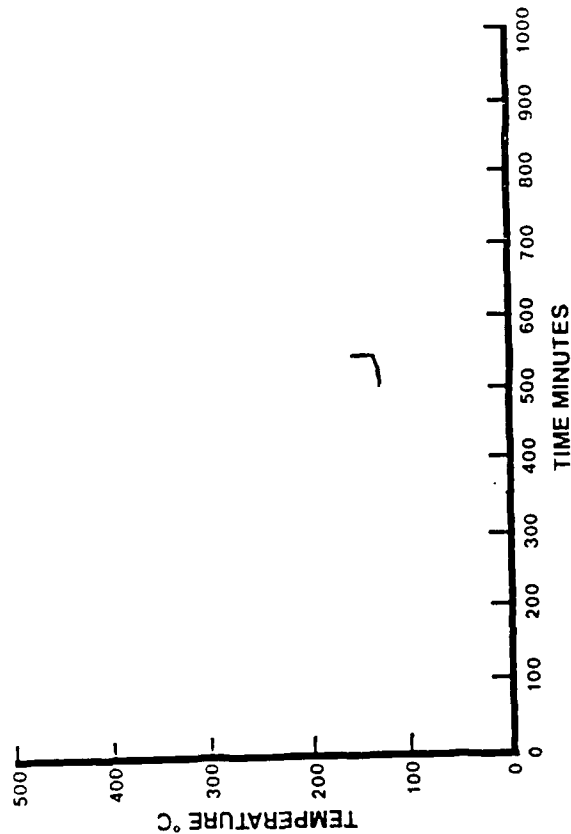


FIG 7 LP101 IN GLASS-LINED BOMB

TEMPERATURE vs TIME PLOT

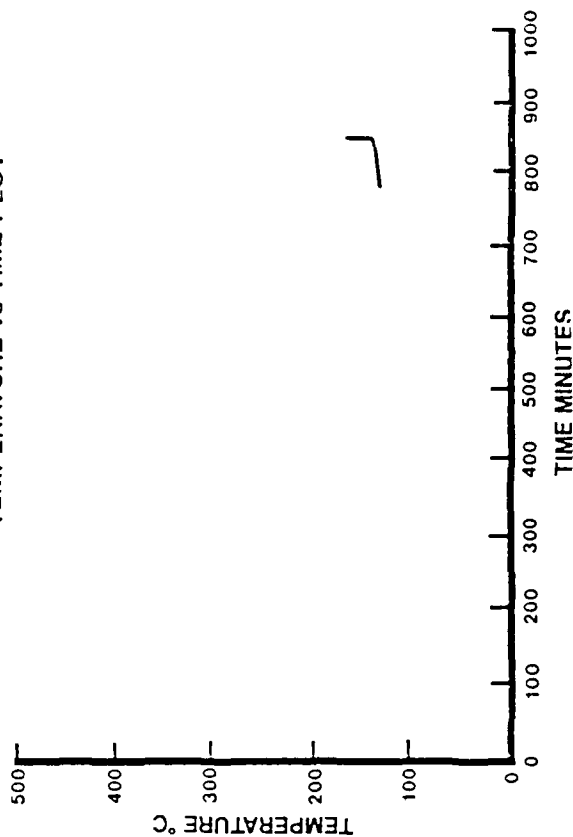


FIG 6 LP101 IN GLASS-LINED BOMB

TEMPERATURE vs TIME PLOT

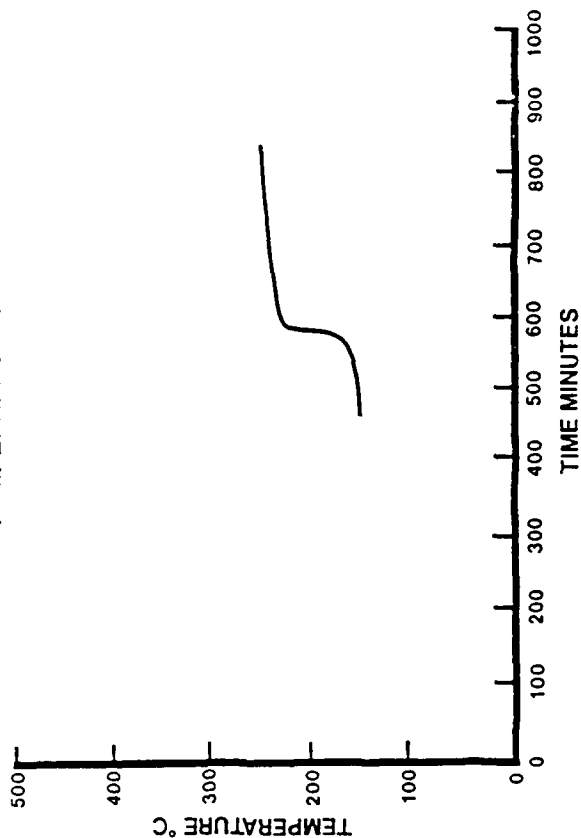


FIG 8 IPN IN SPHERICAL TITANIUM BOMB



TEMPERATURE vs TIME PLOT

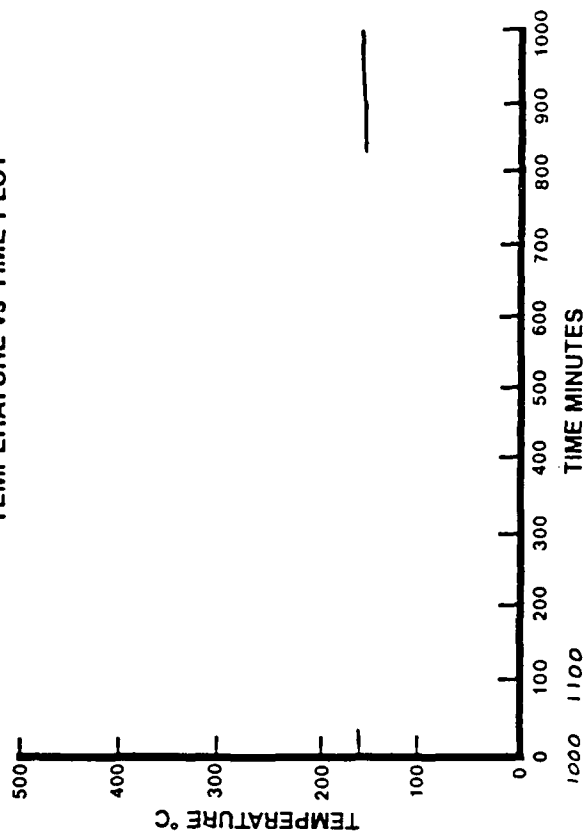
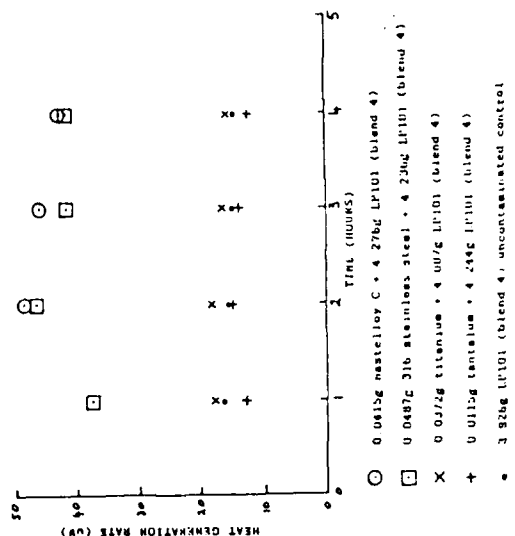


FIG 10 IPN IN GLASS-LINED BOMB



○ 0.0615g hastelloy C + 4.276g LP101 (blend 4)  
 □ 0.0487g 316 stainless steel + 4.230g LP101 (blend 4)  
 X 0.0372g titanium + 4.007g LP101 (blend 4)  
 + 0.0115g tantalum + 4.244g LP101 (blend 4)  
 • 3.826g LP101 (blend 4), uncontaminated control

FIG 12 HEAT GENERATION FROM LP101 SAMPLES THAT HAVE BEEN CONTAMINATED WITH FILLS OF METAL

TEMPERATURE vs TIME PLOT

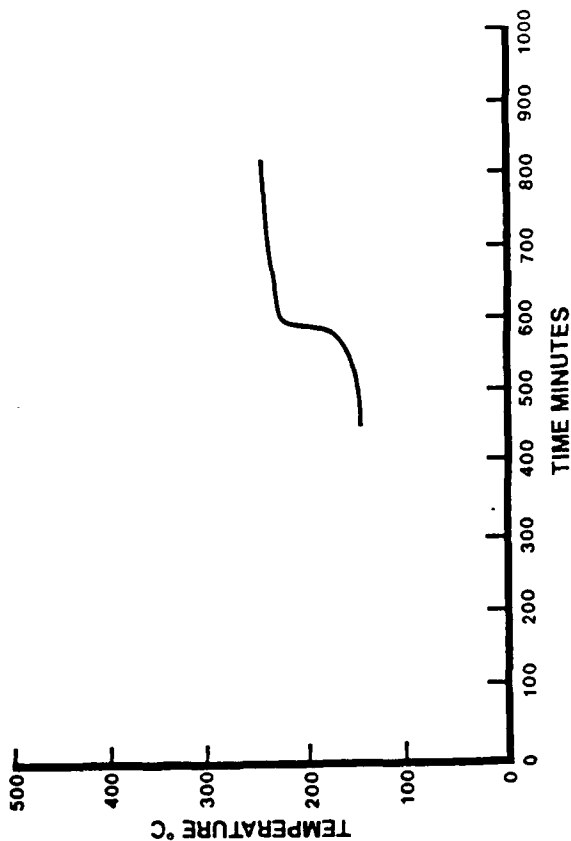


FIG 9 IPN IN SPHERICAL TITANIUM BOMB

TEMPERATURE vs TIME PLOT

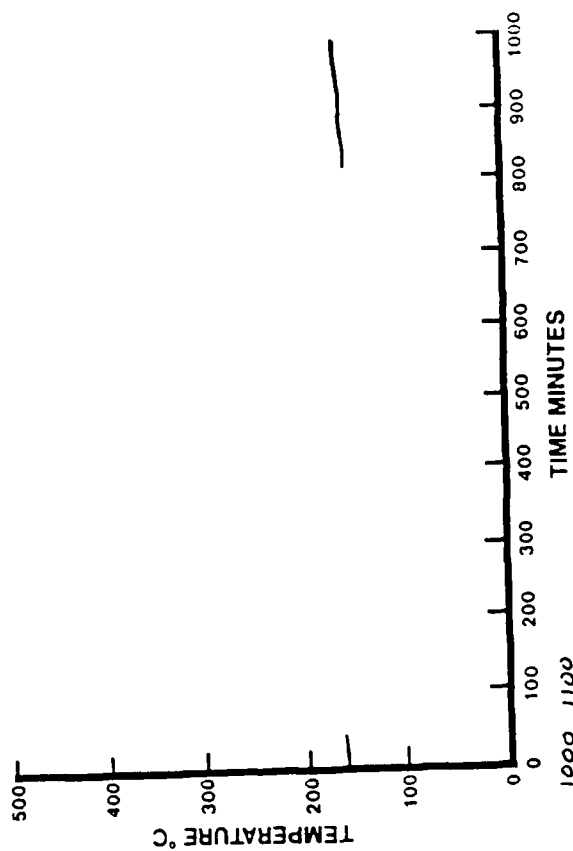


FIG 11 IPN IN GLASS-LINED BOMB

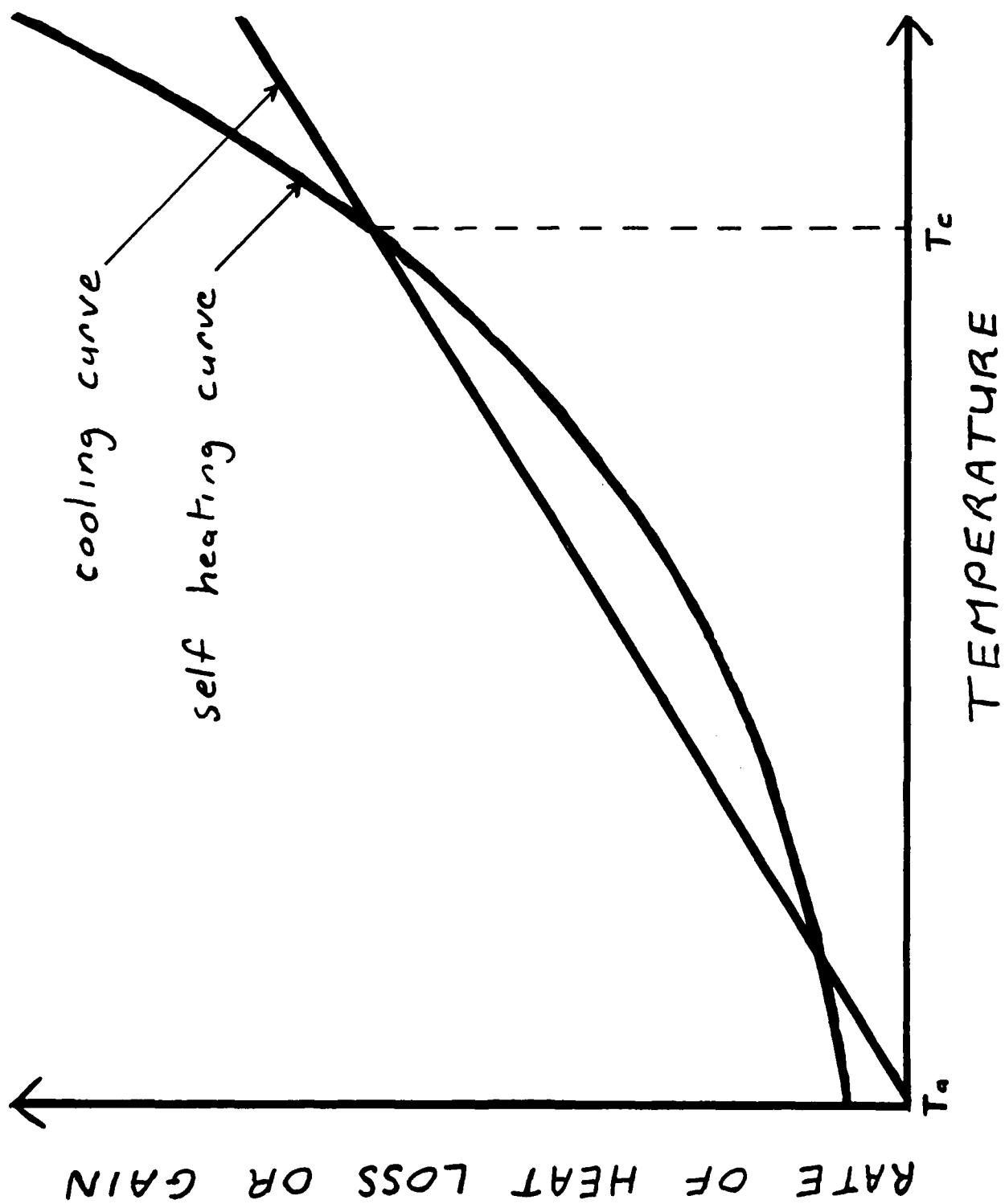
# **The Anomalous Behaviour of HAN-Based Liquid Gun Propellant During Analysis (Part 2, Adiabatic studies)**

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( United Kingdom )**

## AIMS OF THIS PRESENTATION

- 1) Factual description of events
- 2) Highlight certain features
- 3) Practical implications



# Horse dies in freak inferno

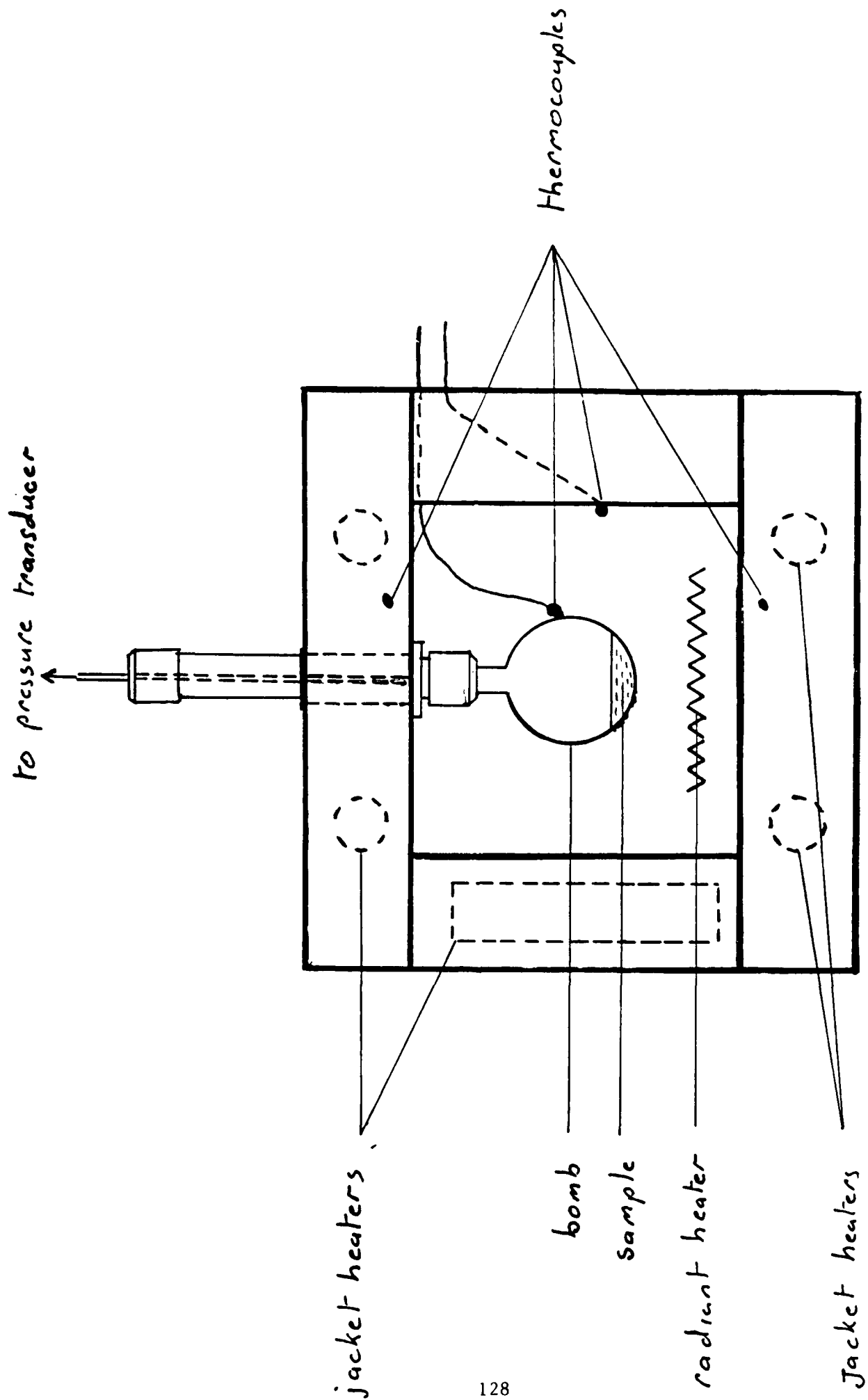
A HORSE was burnt to death when a pile of its own manure burst into flames.

Three other horses were rescued from the stables at Walberton, Sussex.

The alarm was raised late at night when owners Carol and John Harrison heard the animals whinnying with fear.

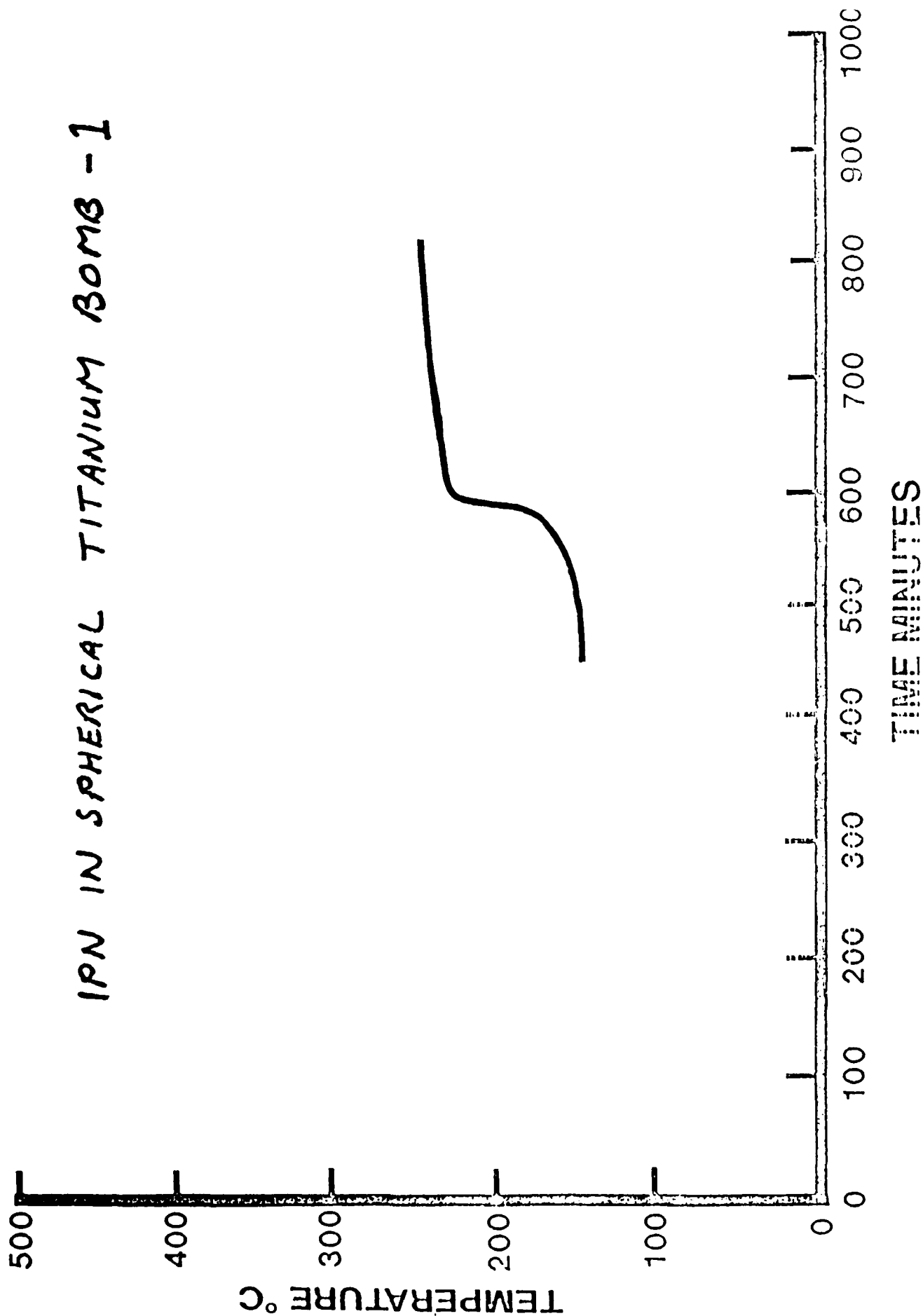
They managed to lead three horses to safety, but the fourth was trapped by the flames.

A fire expert said: "It was a case of spontaneous combustion."



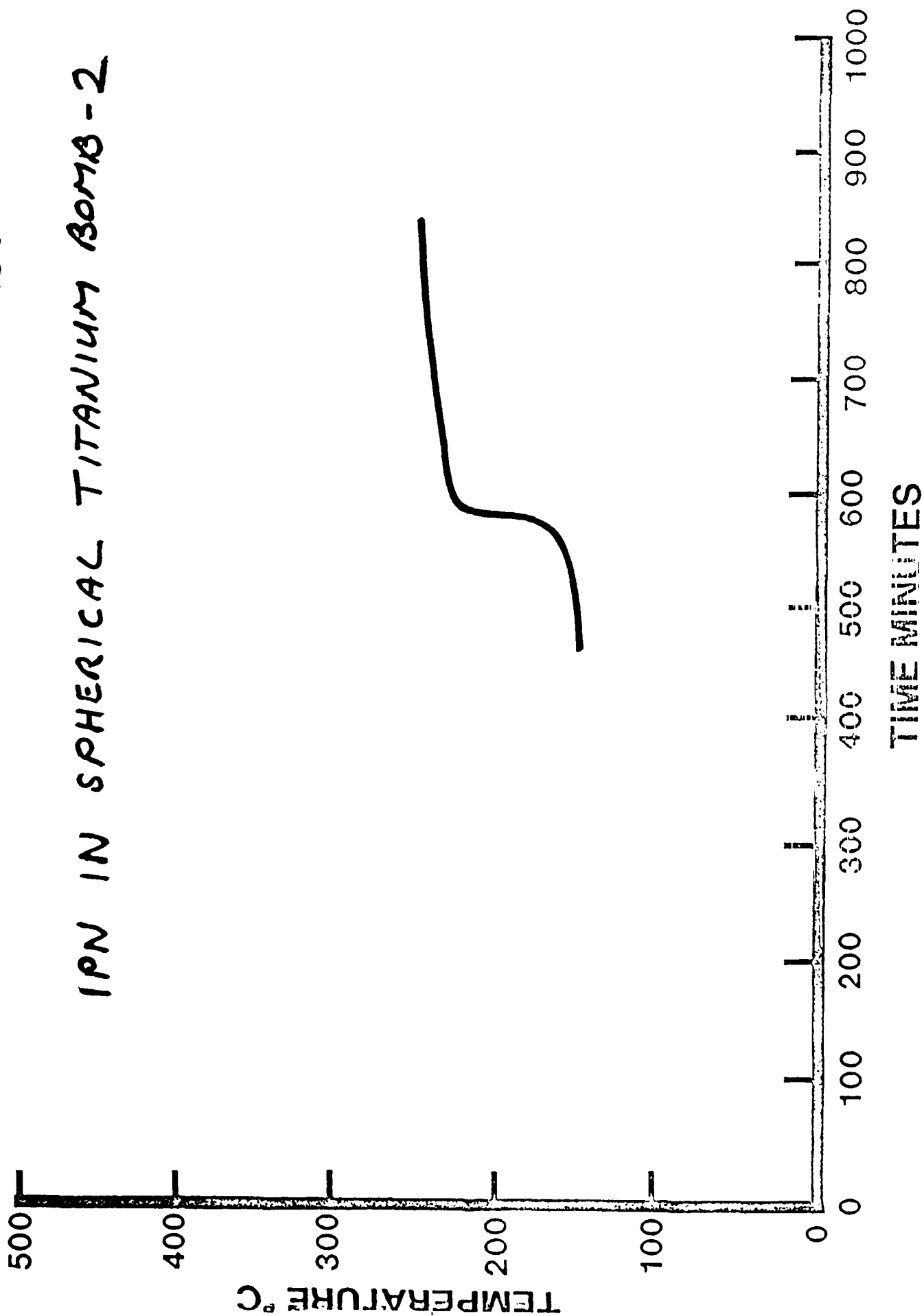
# TEMPERATURE vs TIME PLOT

IPN IN SPHERICAL TITANIUM BOMB - 1



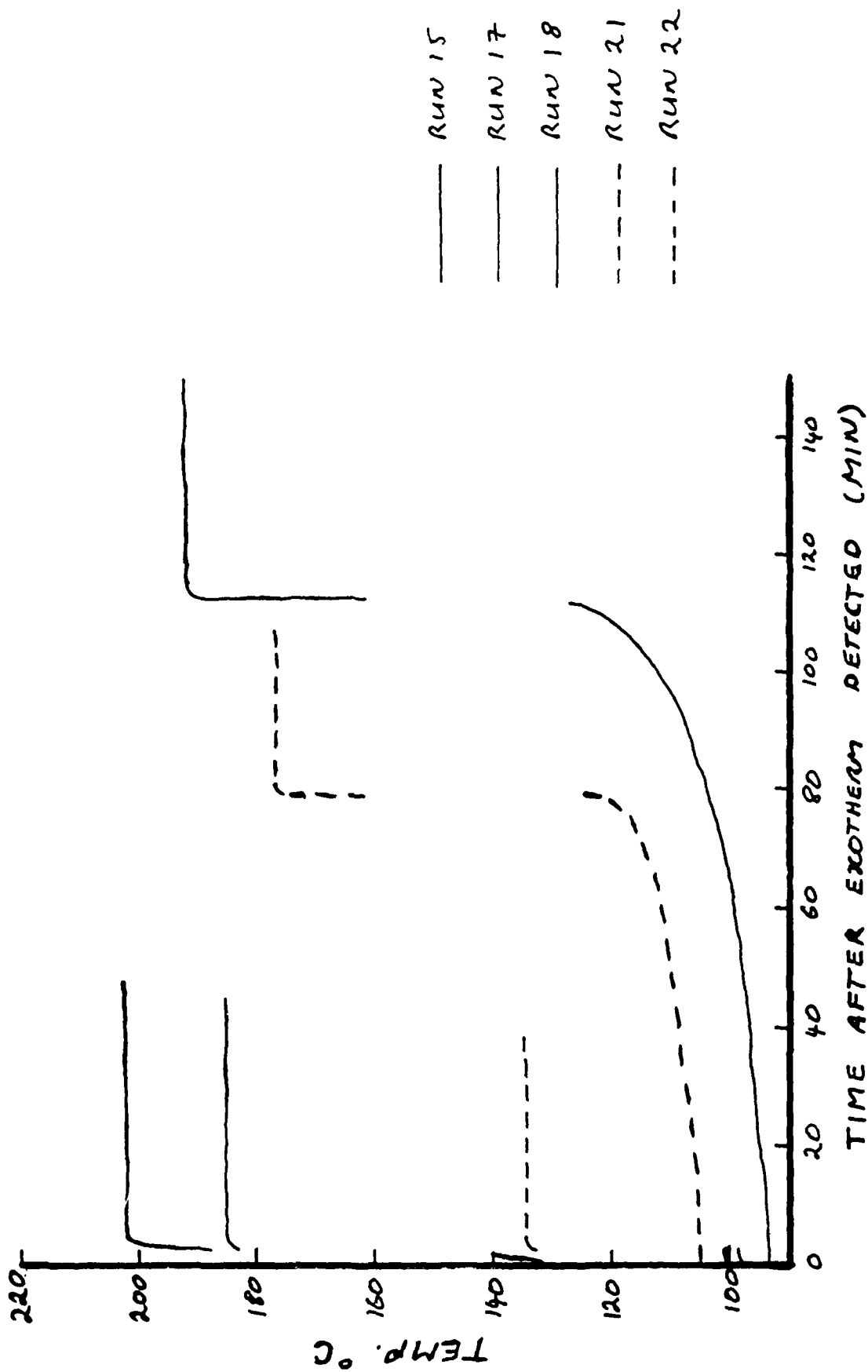
# TEMPERATURE vs TIME PLOT

IPN IN SPHERICAL TITANIUM BOMB-2

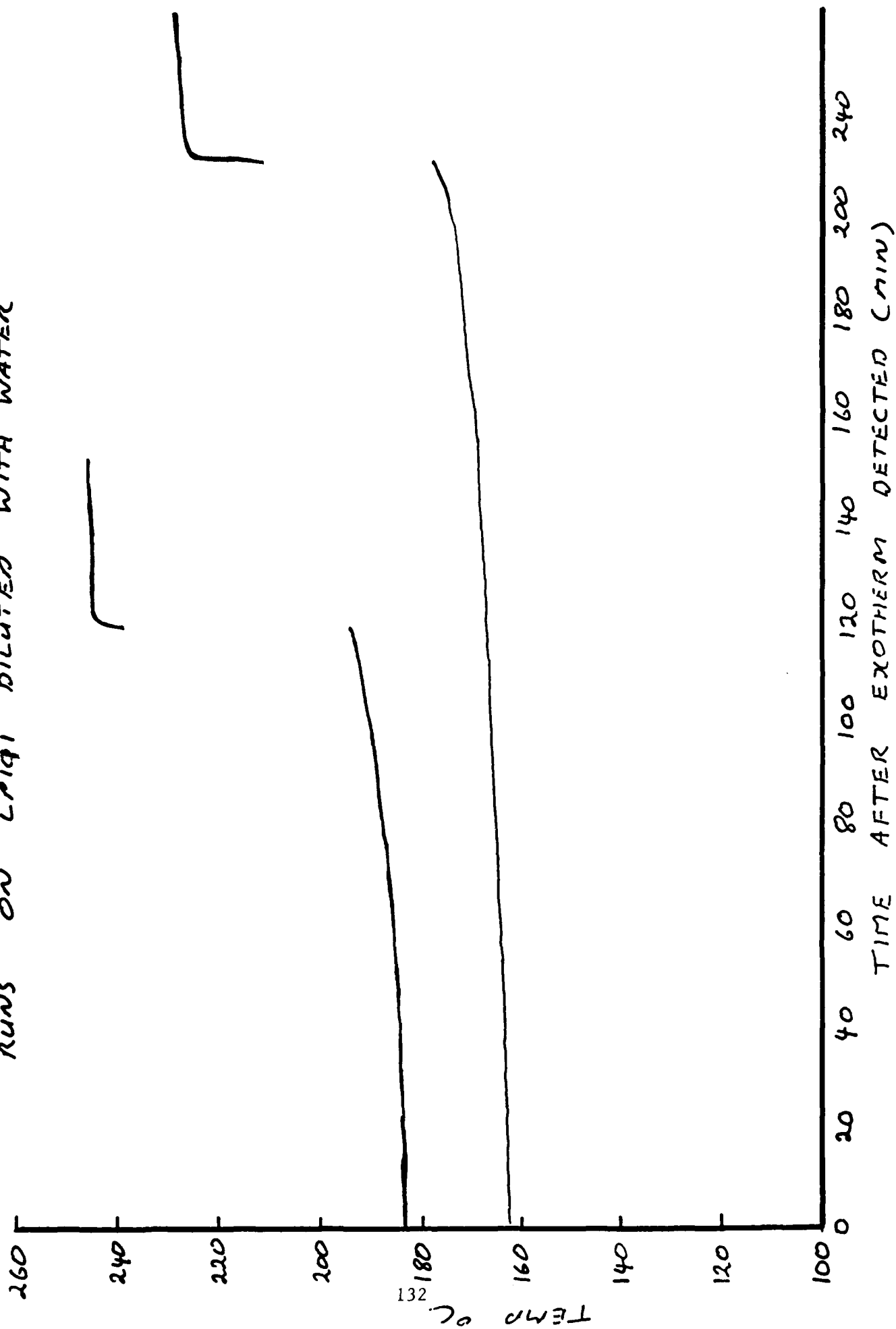


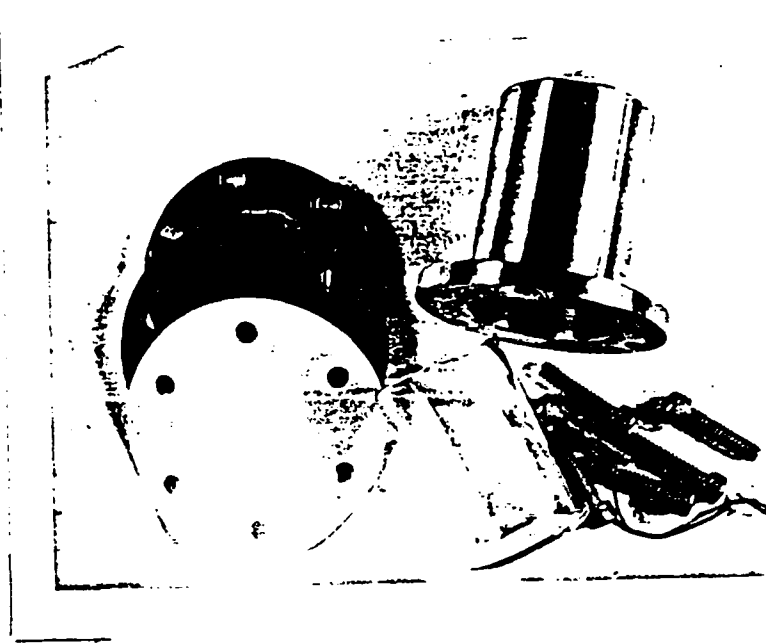


# TEMPERATURE vs TIME PLOTS FROM ARC RUNS ON UNDILUTED LP101

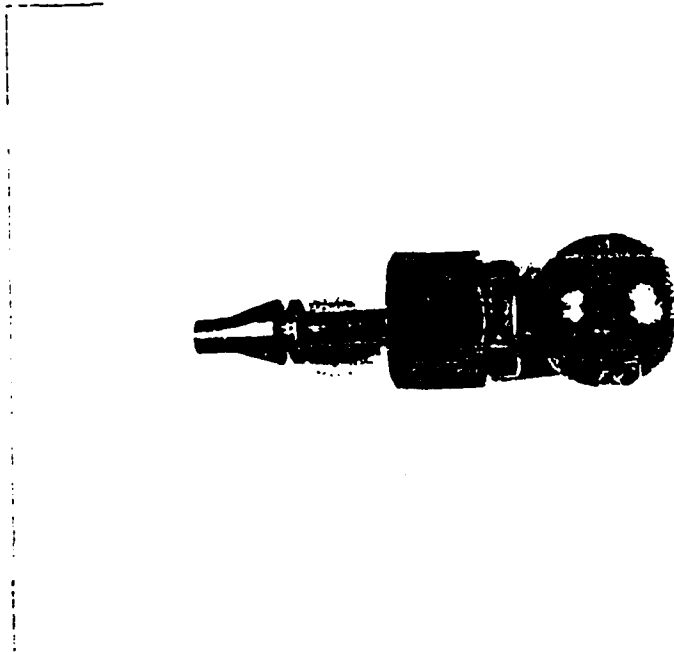


TEMPERATURE vs TIME PLOTS FROM ARC  
 RUNS ON LIQ1 DILUTED WITH WATER



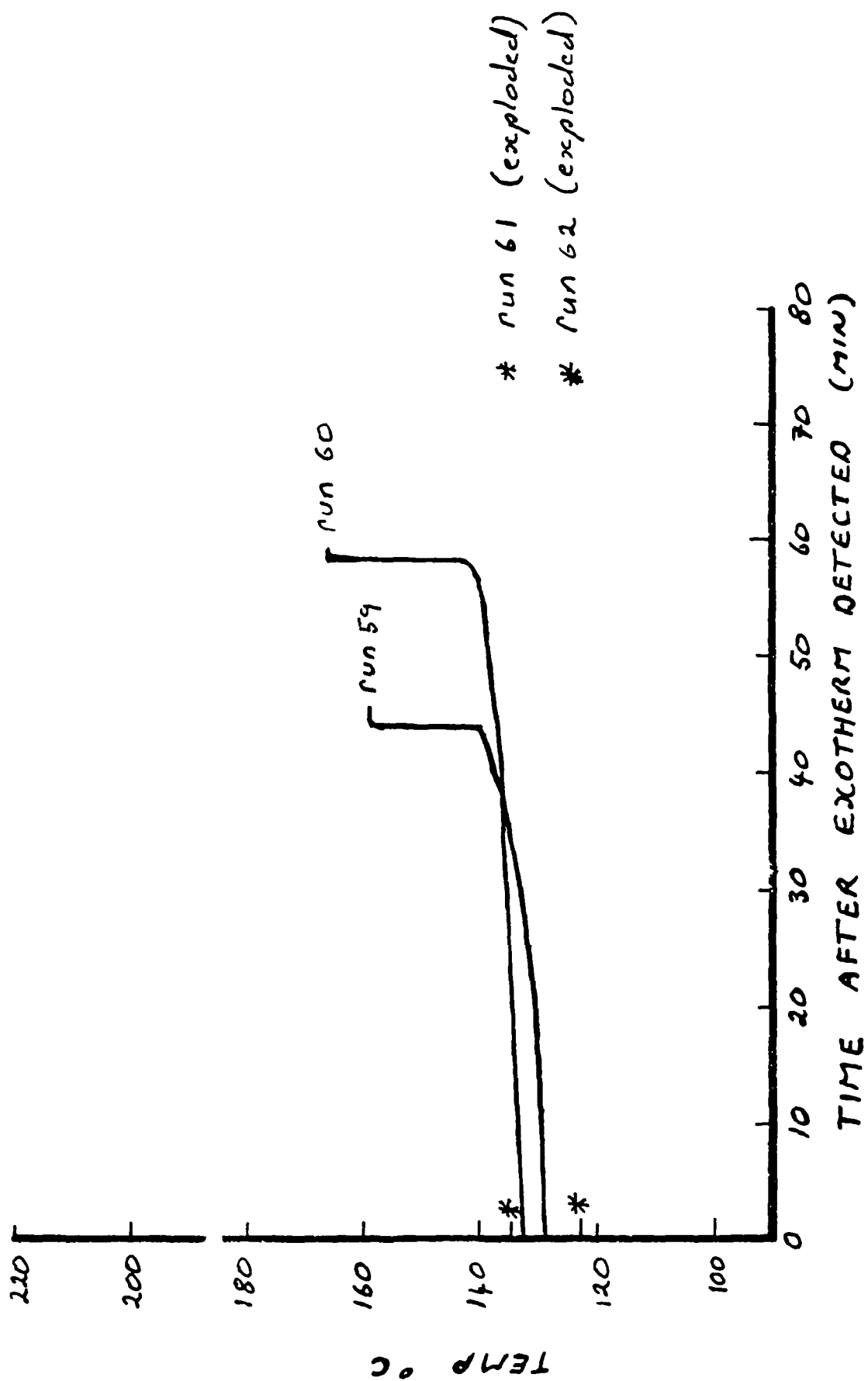


WIDE-MOUTHED BOMB  
(WITH GLASS LINER)



SPHERICAL BOMB

# TEMPERATURE VS TIME PLOTS FROM ARC RUNS ON UNALUTED LAPID IN GLASS-LINED BOMBS



Sample	Bomb Type	Thermal Inertia ( $\phi$ )	Temperature At Which Self-Heating First Detected ( $^{\circ}\text{C}$ )
0.3544g LP101	Titanium	7.14	93
0.1847g LP101	Titanium	4.48	132
0.1604g LP101	Titanium	5.25	101
1.4191g LP101 <sup>c</sup>	Titanium	11.9	162
1.814g LP101 <sup>c</sup>	Titanium	9.7	183
0.1270g LP101	Tantalum	4.81	98.5
0.1302g LP101	Tantalum	5.05	105
0.4898g LP101	Hastelloy C <sup>d</sup>	23.2	129.8
0.4709g LP101	Hastelloy C <sup>d</sup>	24.1	132.6
0.4864g LP101	Hastelloy C <sup>d</sup>	23.4	134.8
0.3577g LP101	Hastelloy C <sup>d</sup>	31.0	123.8
0.2300g LP101 <sup>e</sup>	Hastelloy C <sup>d</sup>	48.3	106.2
0.1868g LP101 <sup>e</sup>	Hastelloy C <sup>d</sup>	58.4	107.0
0.1618g LP101 <sup>r</sup>	Hastelloy C <sup>d</sup>	67.3	113.0
0.1766g LP101 <sup>r</sup>	Hastelloy C <sup>d</sup>	61.8	95.0
0.1025g IPN	Titanium	5.72	149
0.1297g IPN	Titanium	5.65	146
0.1251g IPN	Hastelloy C <sup>d</sup>	104.8	158.5
0.1314g IPN	Hastelloy C <sup>d</sup>	98.6	159.7

<sup>c</sup> 26-28% wt/wt LP101 in water.

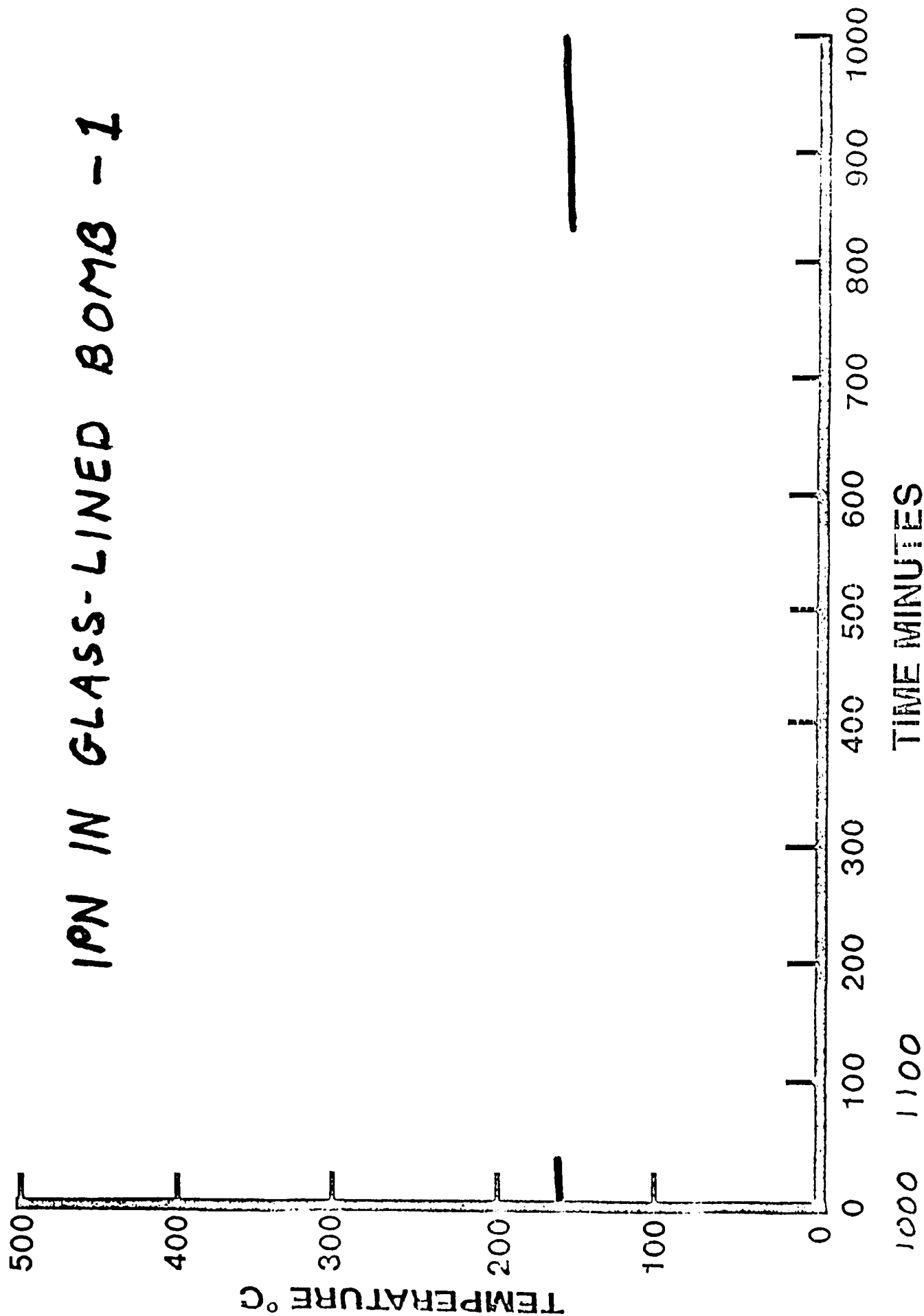
<sup>d</sup> Wide-mouthed bomb lined with an 18x18 mm glass tube.

<sup>e</sup> 2 pieces of 1/8" tantalum tube (0.264g) immersed in propellant.

<sup>r</sup> 2 pieces of 1/8" titanium tube (0.0691g) immersed in propellant.

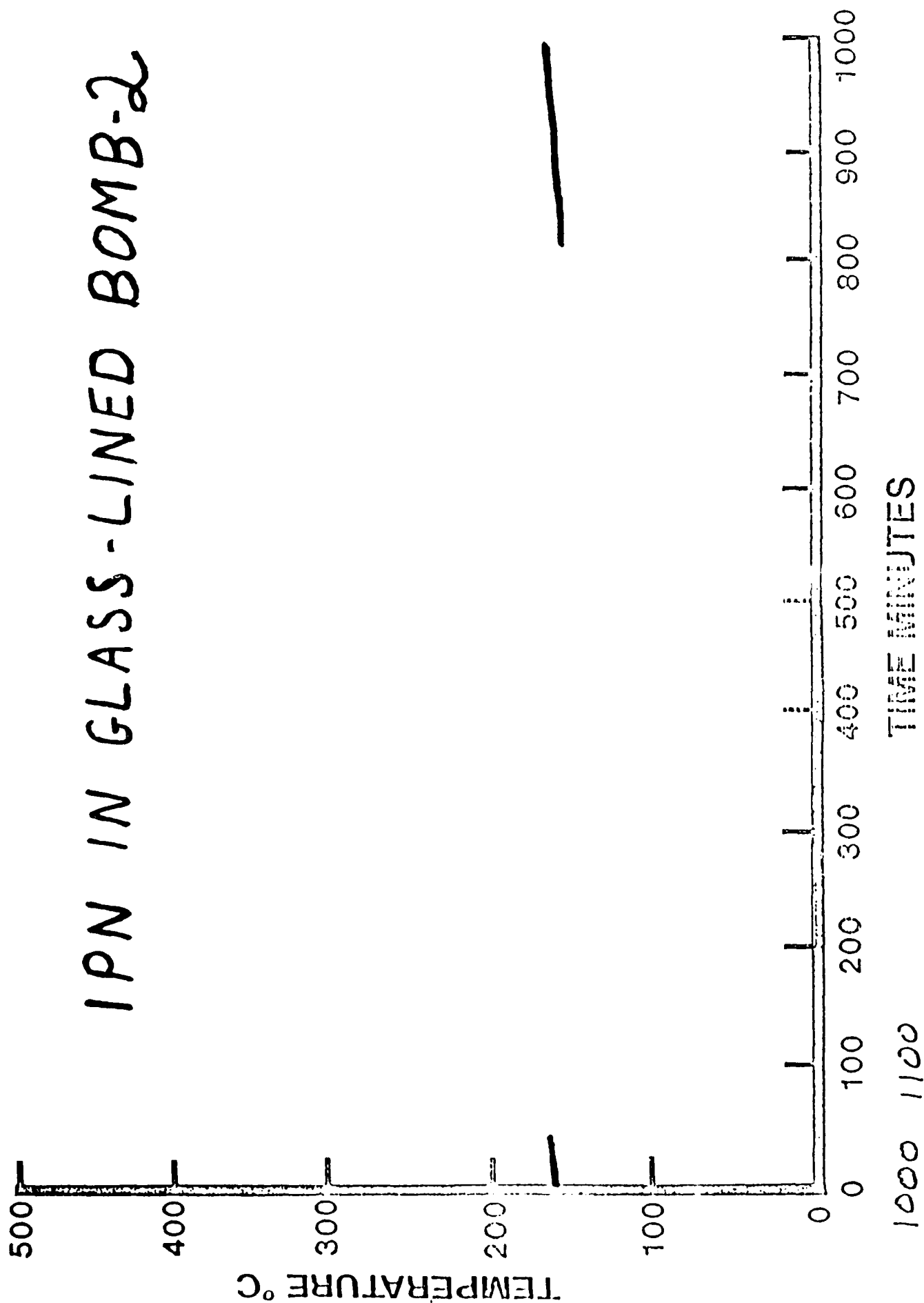
# TEMPERATURE vs TIME PLOT

## IPN IN GLASS-LINED BOMB - 1



# TEMPERATURE vs TIME PLOT

## IPN IN GLASS-LINED BOMB-2



# ARC RUNS ON HAN-BASED PROPELLANT

## -SUMMARY OF OBSERVATIONS

- 1) Not reproducible
- 2) Sudden increase in rate is always seen
- 3) Contact with metals seems to lower the starting temperature of an event
- 4) Some similarity between ARC results and those seen previously with HFC. Therefore the two sets of results may be related.



## POSSIBLE CAUSES OF RAPIDLY INCREASING REACTION RATE

- 1) Thermal explosion
- 2) Slow reaction needs to take place prior to the rapid one.
- 3) Contamination with incompatible solid material covered with a protective layer.
- 4) Branching chain reaction

## FINAL REMARKS

- 1) HAN-based propellant behaviour seems far more variable and unpredictable when analysed by the ARC than other propellants.
- 2) This sort of behaviour would be unacceptable if it occurred in a large mass of propellant.
- 3) Further work is needed to describe, predict and prevent similar events occurring when this propellant is stored in bulk

# RAMAN SPECTROSCOPY OF LIQUID PHASE REACTIONS IN HAN-BASED LPs

R A Beyer and M W Teague  
USA Ballistic Research Laboratory  
APG, MD 21005-5066

## ABSTRACT

An effort is currently underway in our laboratory to devise a diagnostic of the liquid phase reactions of HAN based LPs that will allow us to follow both the original reactants and subsequent liquid phase products. One goal is to make the technique useable up to 1500 psi. Studies are to be undertaken to study the LPs and constituents under various conditions of heating. Heat sources include thermal contact and laser heating (both visible and infrared).

The two main approaches are heating in bulk and heating in a flowing jet of liquid. The first case is more conventional, although rapid data acquisition will be necessary. In the second case, flow velocity will be sufficiently rapid to provide resolution of the reactions. In both cases the elimination of scattered laser light due to bubbles formed in reaction is a major difficulty.

Studies to date have been severely limited by equipment problems. Preliminary observations have been encouraging in the use of fiber optics for collecting the Raman signals. Raman signals have been obtained in a variety of configurations for the initial components; no measurements of products have been made to date. Some preliminary measurements of low-energy modes near 200cm<sup>-1</sup> have been made using a colloidal crystalline filter to remove scattered laser light.

# **RAMAN SPECTROSCOPY OF LIQUID PHASE REACTIONS IN HAN-BASED LPs**

**R A BEYER AND M W TEAGUE  
USA Ballistic Research Laboratory  
APG, MD 21005-5066**

**5th ANNUAL CONFERENCE ON HAN-BASED  
LIQUID PROPELLANT PROPERTIES  
22-23 AUG 1989**

# APPROACH:

CW Raman Spectroscopy

Various Sample configurations:

Bulk

Drop on Fiber

Jet

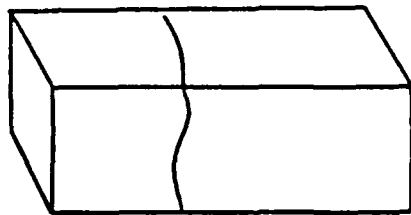
Capillary

Heat Sources:

Hot wire

Laser – visible and infrared

**BULK**



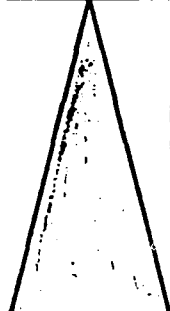
**JET**

NOZZLE →



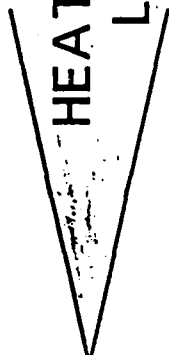
FLOW ⇄

PROBE  
LASER



HEAT

LASER



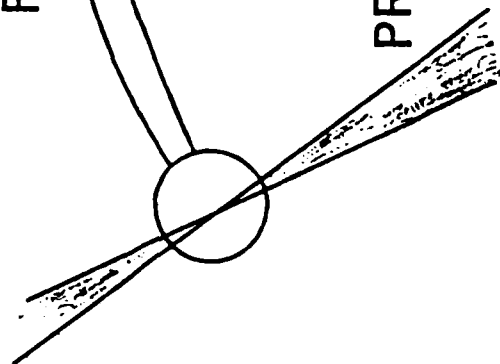
THIN JET  
OF LIQUID

## DROP ON FIBER

FIBER OPTIC



PROBE LASER



→  
SIGNAL TO  
SPECTROMETER

# SUMMARY OF OBSERVATIONS

Nitrate and Water signals observed in  
all configurations

Heating difficult in jet — insufficient power

Drop on fiber looks promising

Optical filter required for reduction of  
scattered light for any technique

# ELIMINATION OF SCATTERED LASER LIGHT

TRIPLE MONOCHROMATOR

CRYSTALLINE COLLOIDAL FILTER

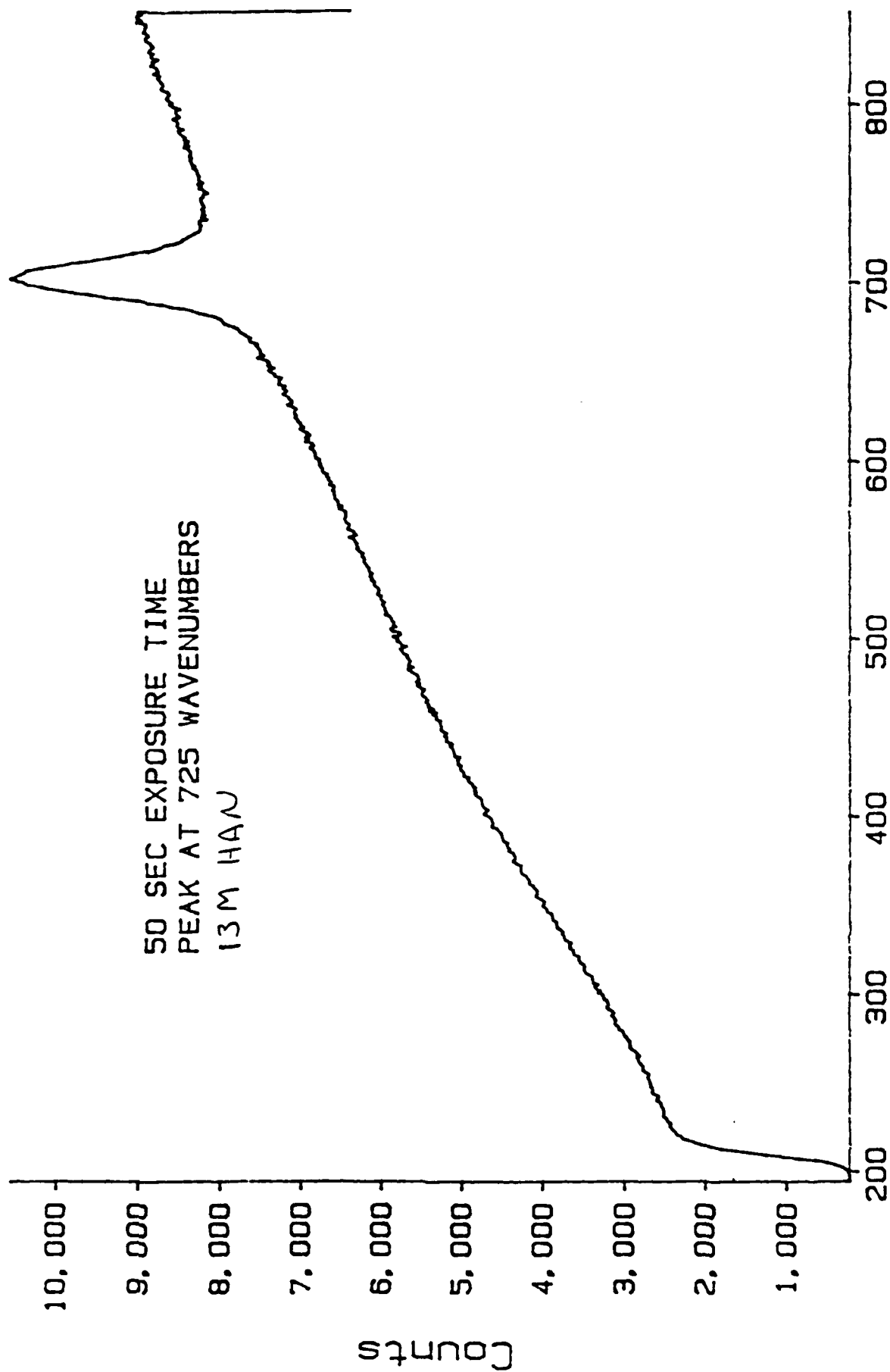
BRAGG DIFFRACTION BY ORDERED  
ARRAY OF SPHERES

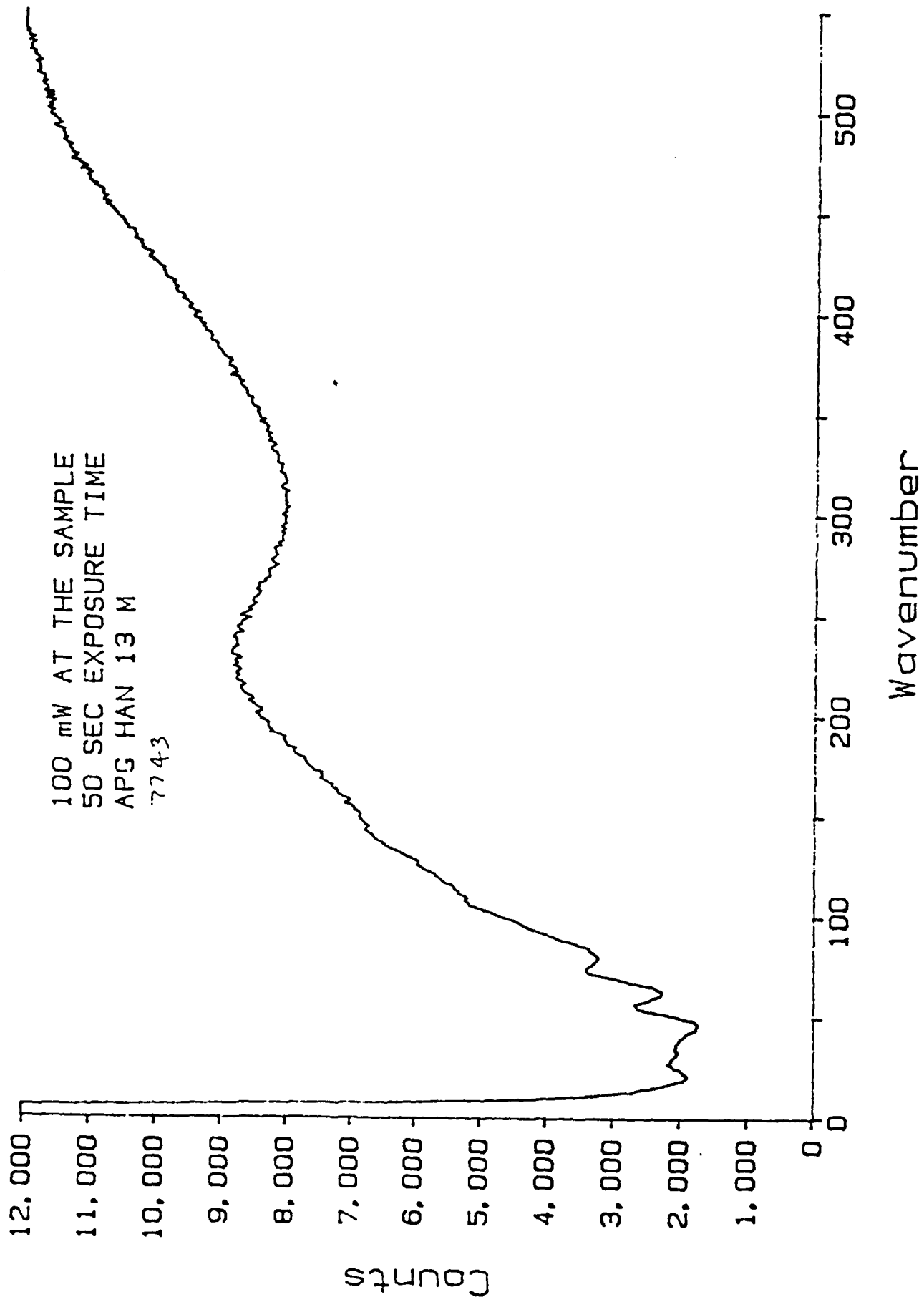
OPTICAL DENSITY  $\sim 10^4$  OVER 5nm

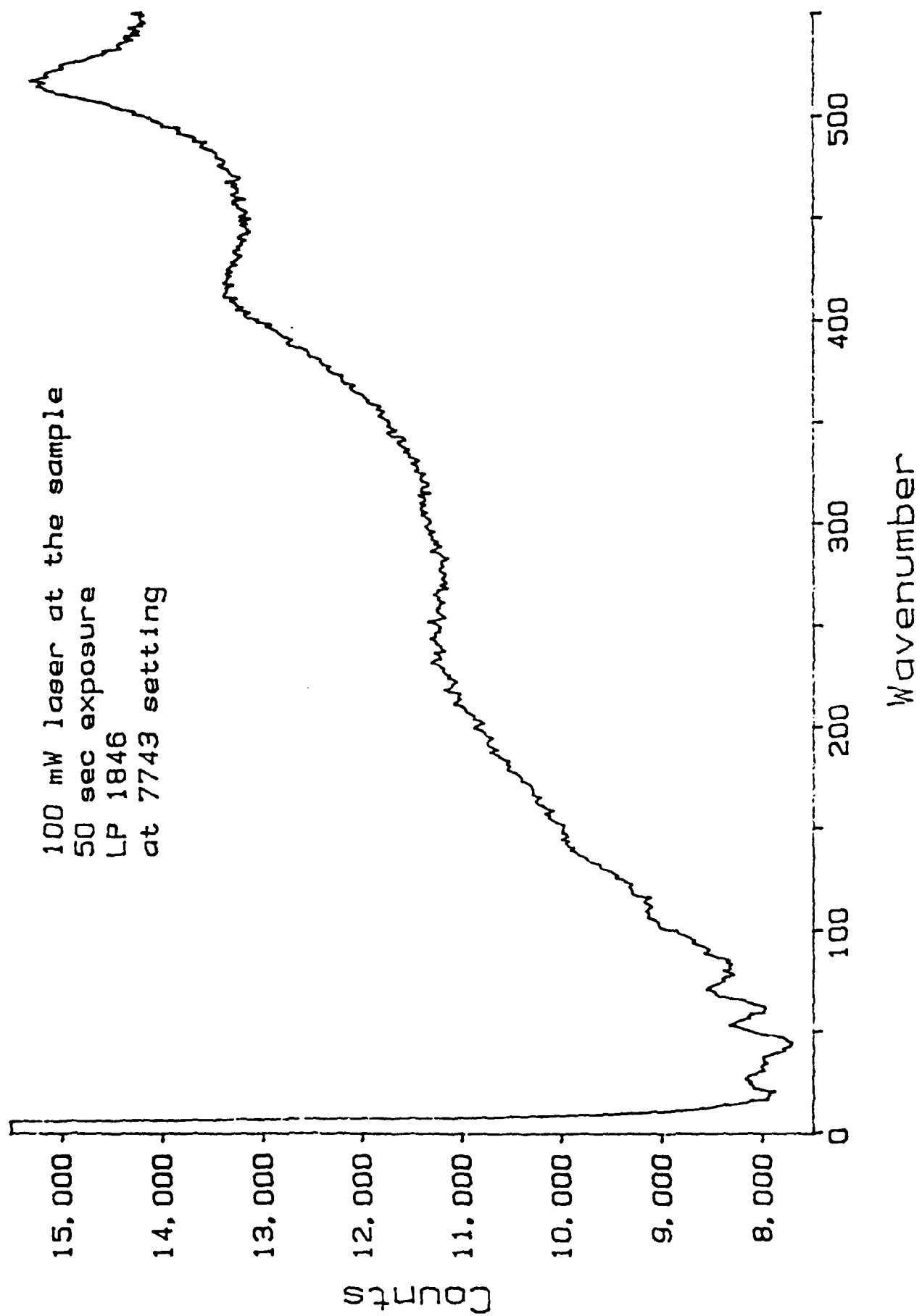
PROVIDES SIMPLE SYSTEM FOR RAMAN STUDIES



L Mem: 1, Trk: 1, C: 522, cm-1: 790.875, Magnitude: 8.546







## Nonlinear Spectroscopy of Water Droplets Containing Nitrates\*

Richard K. Chang, Ali Serpenguzel, and Paul Chen  
Yale University  
Section of Applied Physics and Center for Laser Diagnostics  
New Haven, Connecticut 06520

Optical diagnostic techniques to determine the chemical species and physical properties of multicomponent liquid droplets are essentially nonexistent. We have been developing a nonintrusive, in-situ nonlinear optical technique which has the potential of providing both chemical and physical information about liquid propellant droplets. Because of the unique properties of droplet morphology, this technique is particularly applicable to droplets but less applicable to the gas surrounding the droplets.

There are two consequences of the spherical droplet morphology. First, the spherical droplet illuminated face concentrates the incident laser radiation in a region just within the droplet shadow face and causes nonlinear optical interactions to take place there. Second, the spherical liquid-air interface causes the droplet to act as a high Q optical cavity, which is capable of providing efficient optical feedback for the internally generated Raman radiation. When the round-trip Raman gain exceeds the round-trip loss at the Raman wavelength, stimulated Raman scattering (SRS) results.

The SRS frequency shifts from the incident laser frequency are signatures of the vibrational frequencies of the molecules and can, therefore, be used to identify the molecules. We have been investigating SRS from water droplets containing 1 to 1.5 M  $\text{NO}_3^-$  and in some cases also containing 1 to 1.5 M  $\text{SO}_4^{2-}$ .

We will review what we have learned about laser-induced electrostrictive shape distortions of water droplets containing  $\text{NO}_3^-$  and the time delay in the growth of the first-order  $\text{NO}_3^-$  Stokes SRS and of the multiorder  $\text{NO}_3^-$  Stokes SRS. We will present our new results obtained from a spray of water droplets containing 1.5 M  $\text{NO}_3^-$  and 1.5 M  $\text{SO}_4^{2-}$ . Only a few of the larger droplets in the spray produced strong SRS signals. Calculations based on the Lorenz-Mie theory indicate how Q decreases as the droplet radius decreases and as the liquid index of refraction approaches that of the surrounding gas (i.e., the critical condition). In an attempt to relate the SRS intensity to the chemical concentration within the droplet, we will present new results on the SRS intensity fluctuations with single-mode and multimode laser excitation.

\*This work was supported in part by ARO Contract No. DAAL03-87-K-0076.

## SHOCK TUBE IGNITION OF TEAN IN NITROUS OXIDE

Richard A Beyer  
US Army Ballistic Research Laboratory  
APG, MD 21005-5066

### ABSTRACT

While many studies of the decomposition of the liquid propellant components HAN and TEAN have been performed, little attention has been given to the possible role of ignition of these materials in the earlier decomposition products. In particular, since HAN decomposes significantly earlier than TEAN, it is possible that the TEAN reactions are dominated by oxidation by HAN products. For this study, the possible reaction of TEAN with nitrous oxide ( $N_2O$ ) has been the focus.

In order to provide hot  $N_2O$  without decomposing it into nitrogen and oxygen species, a shock tube was used. Kinetic modeling studies were carried out to ensure that the  $N_2O$  would remain unreacted for times long compared with the shock tube test times. Thus we are able to immerse the TEAN into a bath of  $N_2O$  which is made "instantaneously" hot. In these experiments, the TEAN is mounted on a post near the end of the shock tube. Early experiments were done with a simple mount; however, the hygroscopicity of the TEAN made it necessary to heat the samples under vacuum in the shock tube to drive off water.

In these experiments, pressure and light emission are recorded. The light emission should be indicative of ignition, or at least an increase in temperature, assuming that emissivity stays the same. Early experiments showed large light output, indicative of full ignition. Since that time, less reaction has been observed. Further studies using air as the oxidizer have shown evidence of significant reaction, but no full ignition.

These observations are still very preliminary, and need to be refined. In addition to pursuing these measurements to a point of understanding, the addition of convective heating and the study of other TEAN mixtures are anticipated.

# SHOCK TUBE IGNITION OF TEAN IN NITROUS OXIDE

RICHARD A BEYER

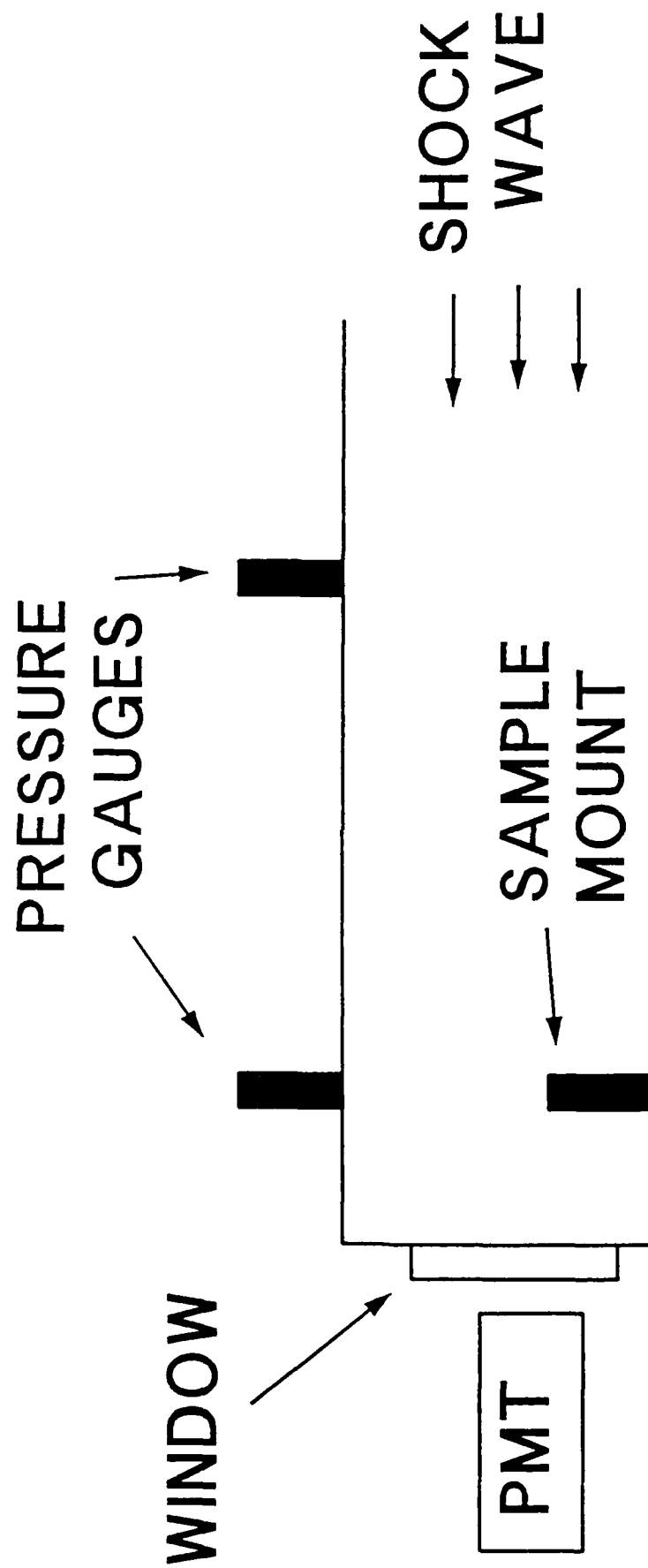
USARMY BALLISTIC RESEARCH LABORATORY  
SLCBR-IB-I  
APG, MD 21005-5066

5th ANNUAL CONFERENCE ON HAN-BASED  
LIQUID PROPELLANT PROPERTIES  
22-23 AUGUST 1989

# BACKGROUND

EVIDENCE THAT HAN DECOMPOSES FIRST  
TEAN MAY THEREFORE BE OXIDIZED BY  
HAN PRODUCTS (eg. N<sub>2</sub>O)

NO DATA ON TEAN IGNITION/COMBUSTION  
AVAILABILITY OF SHOCK TUBE



# SHOCK TUBE TEST SECTION



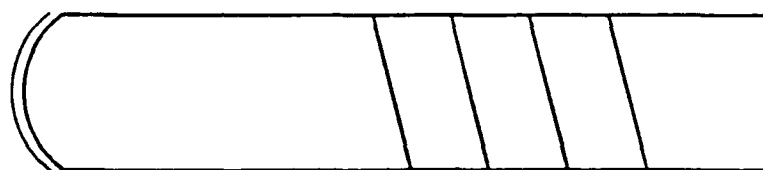
# SAMPLE MOUNTING

TEAN  
CRYSTAL



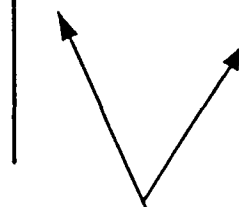
1/8 in. DIA  
SS ROD

TEAN  
(layer)

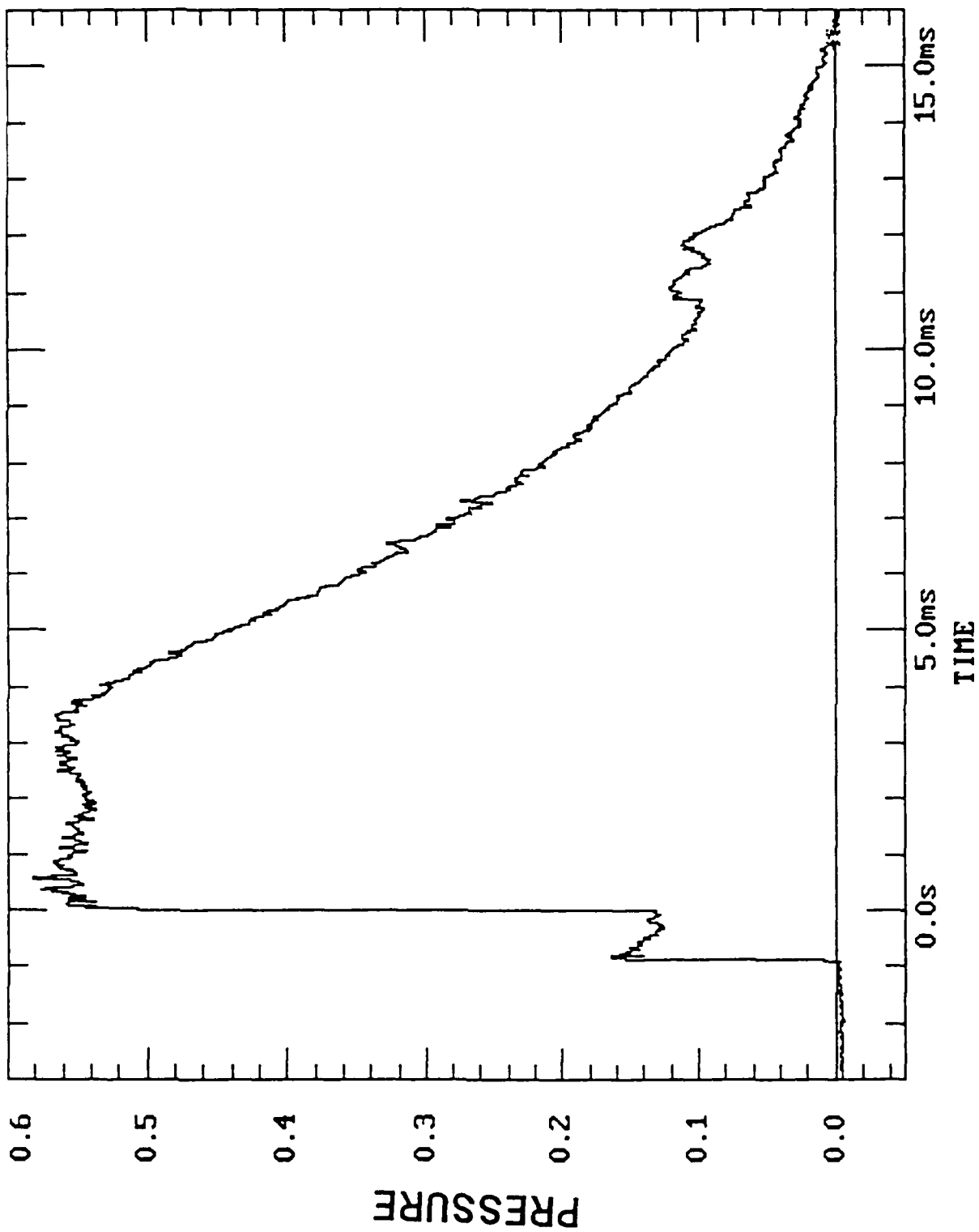


1/8 in. DIA  
SAPPHIRE ROD

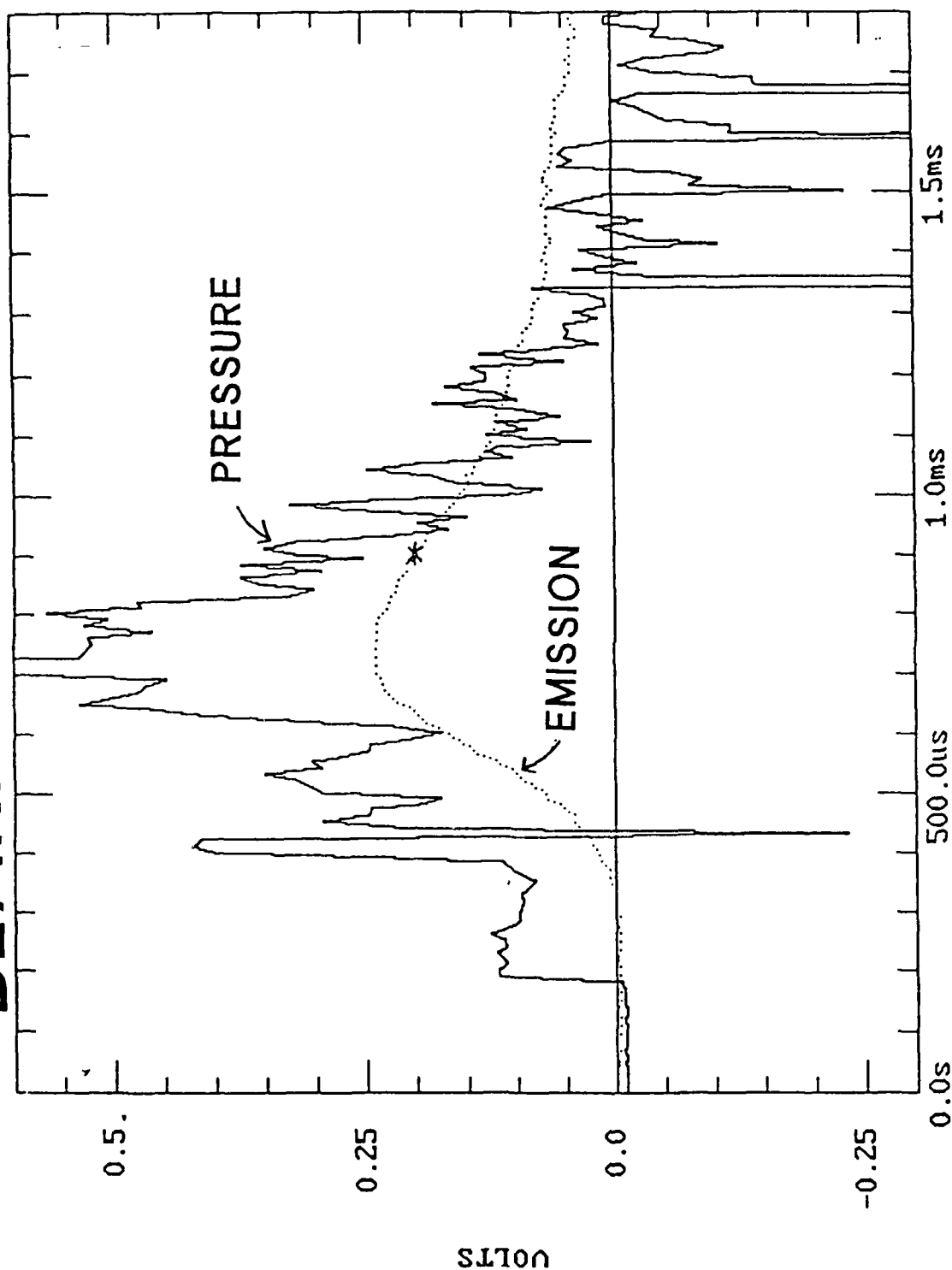
HEATER  
WIRE



# TYPICAL SHOCK BEHAVIOR



# BLANK N2O SHOCK



SHOCK

TEMP = 710 K

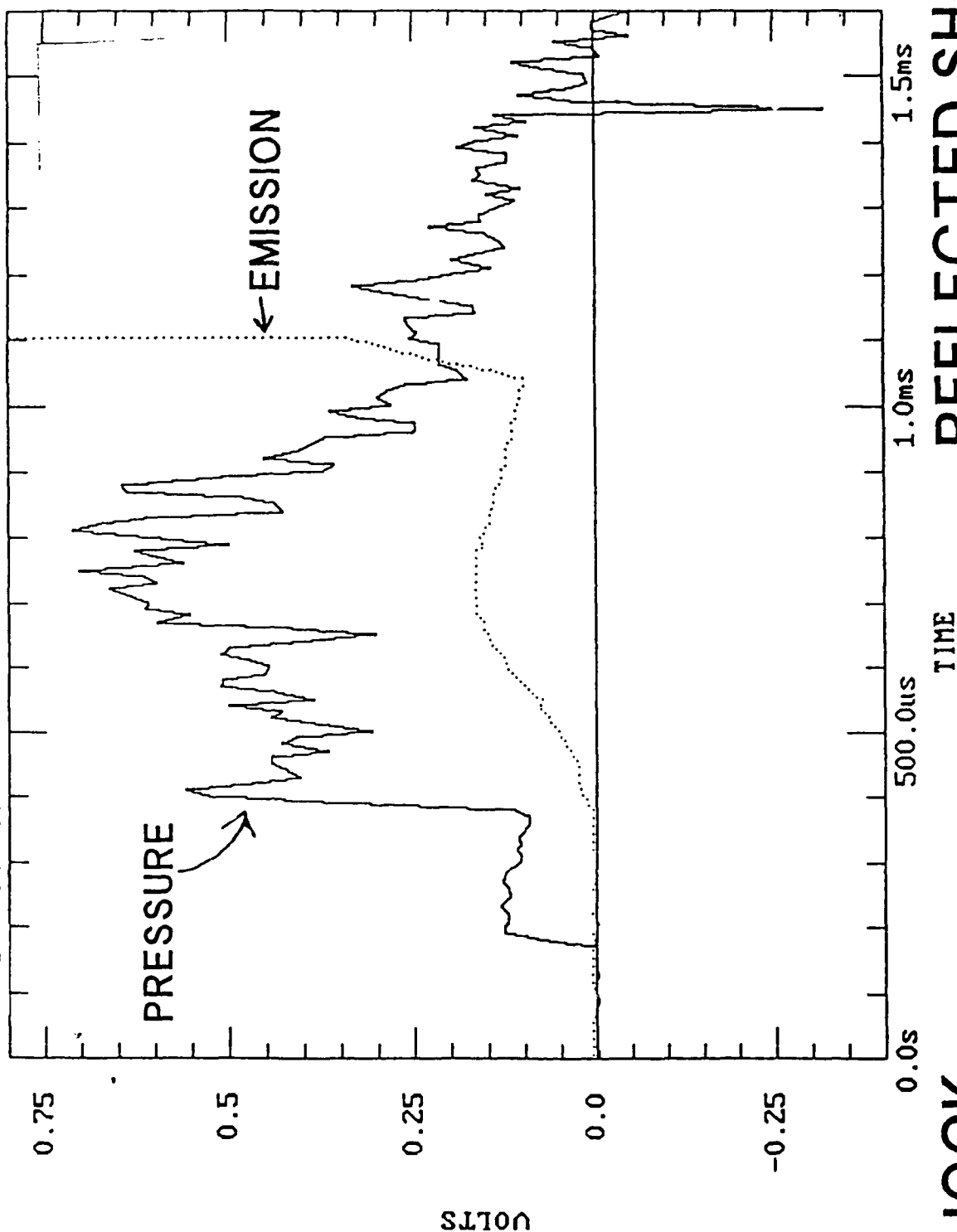
PRESS = .7 ATM

REFLECTED SHOCK

TEMP = 1100 K

PRESS = 5 ATM

# TEAN IN N2O SHOCK



## SHOCK

TEMP = 710 K

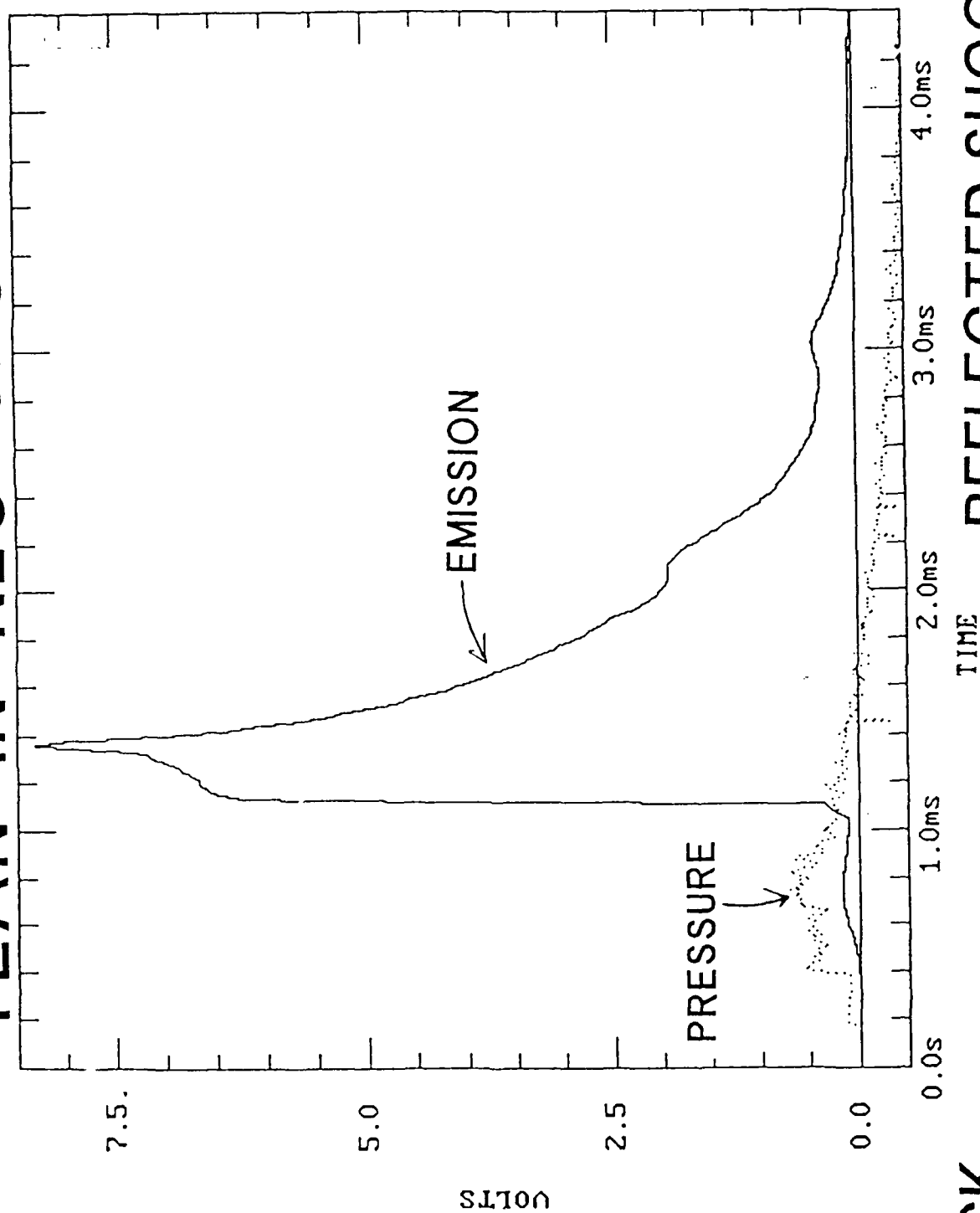
PRESS = .7 ATM

## REFLECTED SHOCK

TEMP = 1100 K

PRESS = 5 ATM

# TEAN IN N2O SHOCK



SHOCK

TEMP = 710 K

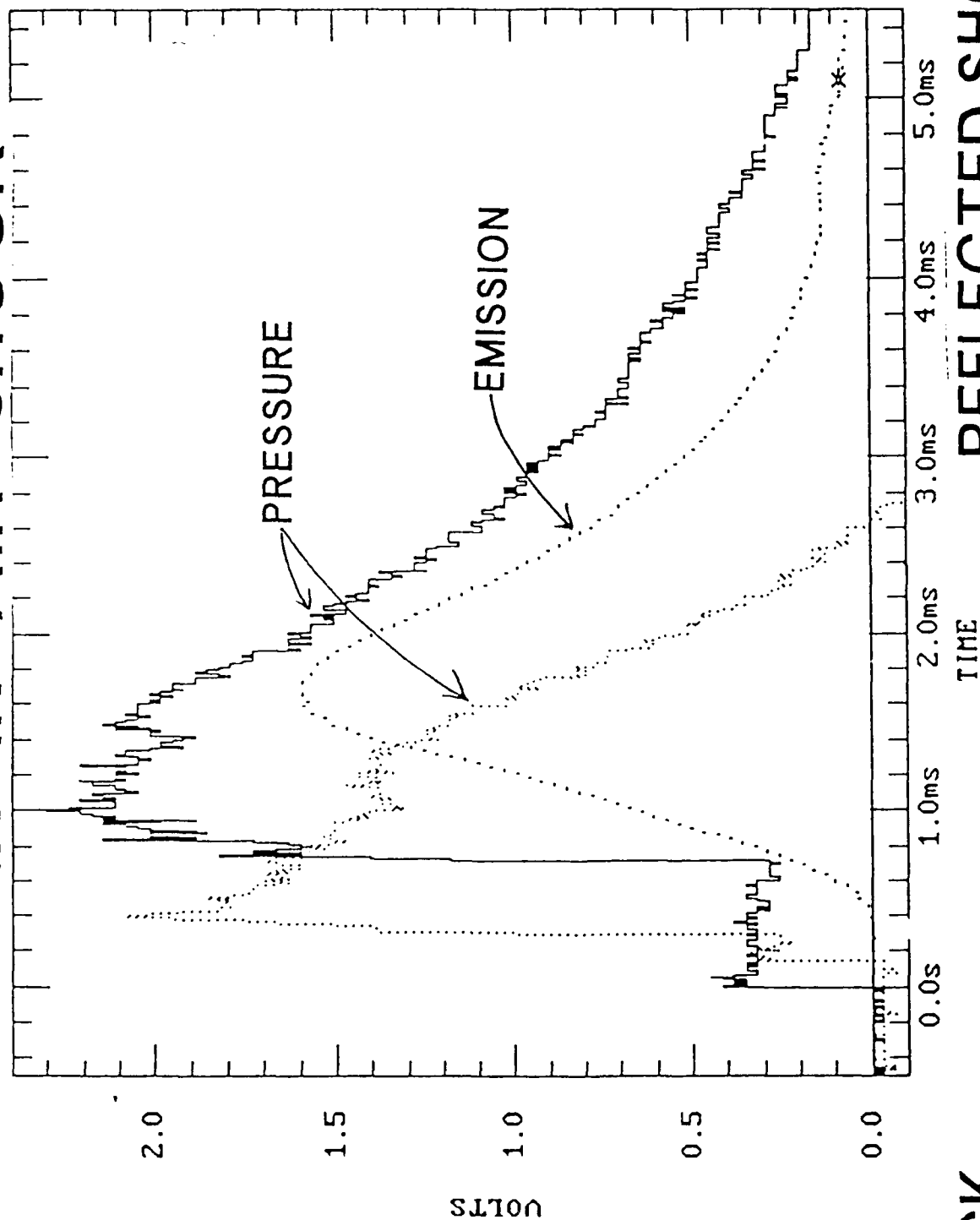
PRESS = 7 ATM

REFLECTED SHOCK

TEMP = 1100 K

PRESS = 5 ATM

# TEAN IN AIR SHOCK



## SHOCK

TEMP = 1160 K

PRESS = 0.75 ATM

## REFLECTED SHOCK

TEMP = 2000 K

PRESS = 4.6 ATM

## PROBLEMS:

HYDROSCOPICITY OF TEAN

LIMITED TEST TIME IN SHOCK TUBE

LACK OF EXPERIENCE WITH SHOCK TUBE

## FUTURE:

LOWER PRESSURES

CONVECTIVE HEATING

OTHER MIXTURES (eg. TEAN/HNO<sub>3</sub>)

# HYDROXYLAMMONIUM NITRATE-BASED LIQUID PROPELLANT COMBUSTION - INTERPRETATION OF STRAND BURNER DATA AND THE LAMINAR BURNING VELOCITY\*

Steven R. Vosen  
Combustion Research Facility  
Sandia National Laboratories  
Livermore, CA 94551-0969

## ABSTRACT

Measurements have been made of the burning velocity of a hydroxylammonium nitrate-based liquid propellant undergoing combustion in a strand burner. Experiments were conducted at constant pressures of 6.7 to 34 MPa while the propellant was confined in a strand burner with a 1.8 x 1.0 mm rectangular cross section, a size smaller than that used in previous studies. An electric discharge was used to ignite the propellant, which was then observed by high-speed photography. The overall burning velocity in the strand burner was found to be influenced by hydrodynamic effects, resulting in a decrease in the overall burning velocity with an increase in pressure up to 26 MPa. Above 26 MPa instabilities became less important and the burning velocity was independent of pressure, a trend which has not been previously noted. The laminar burning velocity of the propellant was estimated to be 26.7 mm/s at pressures of 30 to 34 MPa. Comparison with other hydroxylammonium nitrate-based liquid propellant burning velocity experiments give a burning velocity of  $S_u = 9.45 P^{0.275}$  ( $S_u$  in mm/s,  $P$  in MPa) for pressures of 1.0 to 100.0 MPa. Also noted for the first time was the quenching of the gas phase flame at a pressure of up to 34 MPa in a 1.8 x 1.0 mm burner.



# **The Effect of Hydrodynamics on HAN-Based Liquid Propellant Combustion**

**Steven R. Vosen  
Energetic Materials Division  
Combustion Research Facility  
Sandia National Laboratories  
Livermore, CA 94550**

**5th Annual Conference on HAN-based Liquid  
Propellant Structure and Properties  
August 22, 1989**

## **Outline of presentation**

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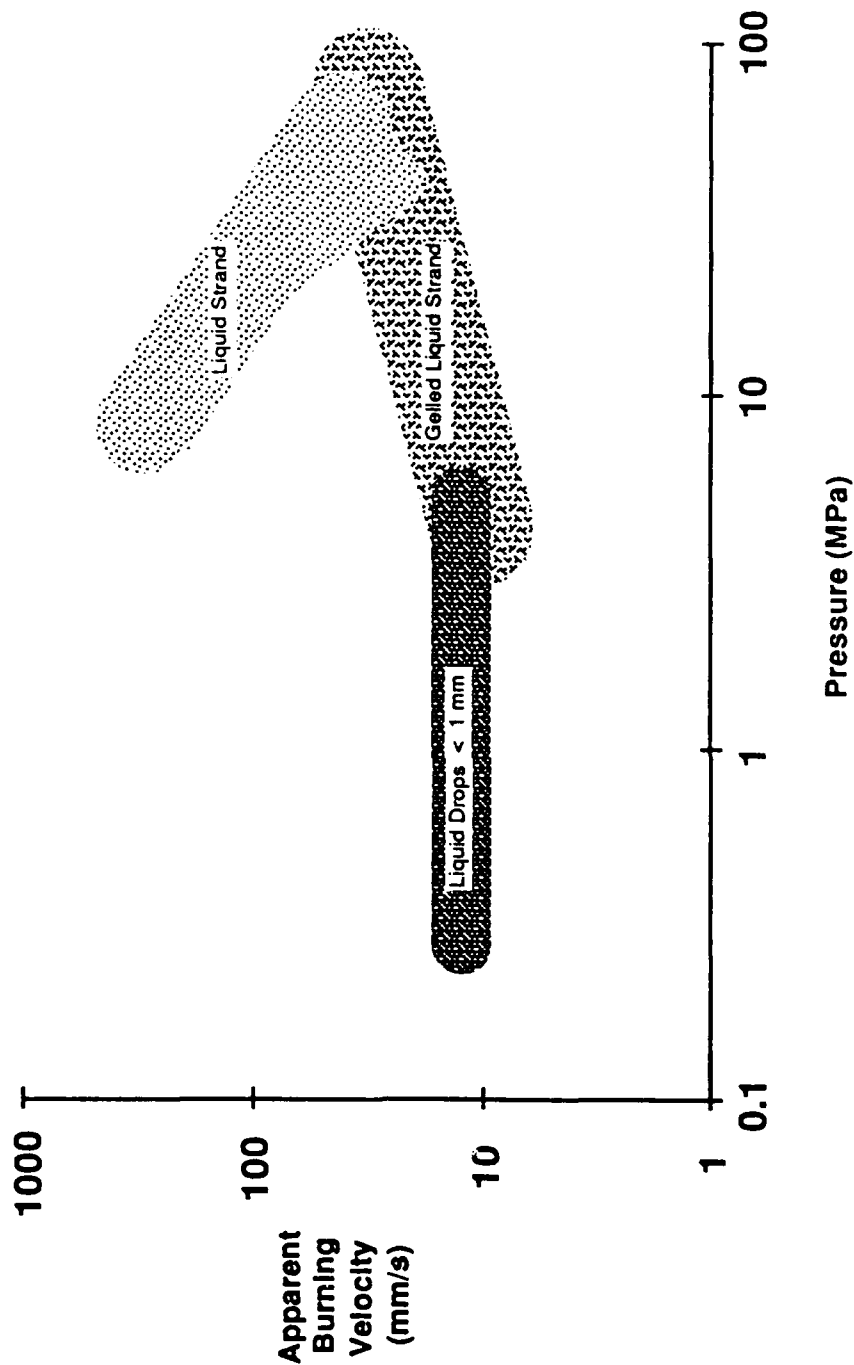
- **Research objectives**
- **Summary of previous results**
- **Background for interpretation of experimental results**
- **Strand Burner Results, LP1846 Burning Velocity**

## **Research objectives**

---

- Determine the cause of the "negative pressure exponent" observed for LP combustion.
- Investigate the role of interfacial instabilities on the burning velocity.
- Determine the importance of gas and / or liquid phase chemistry on LP combustion.

## HAN-LP burning velocity data is inconclusive

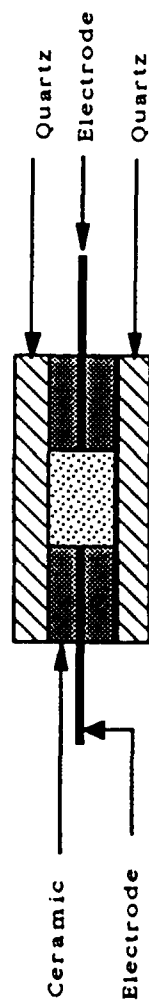


## **Pressure dependence reveals chemical and physical effects**

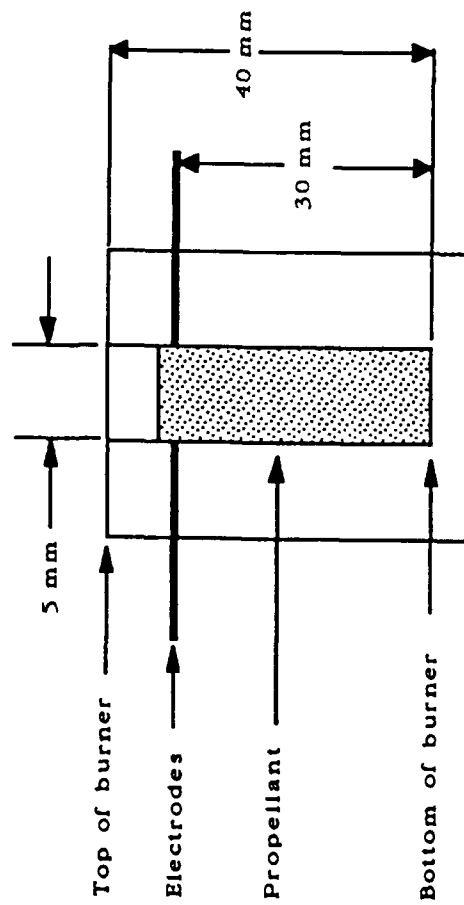
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- The burning velocity pressure dependence is a result of combustion kinetics and physical processes.
- Kinetics: the burning velocity is a function of the thermodynamics and transport properties.
- Physical processes: acceleration, surface tension and viscosity govern liquid-gas interface dynamics.

## Strand burner design provides optical access

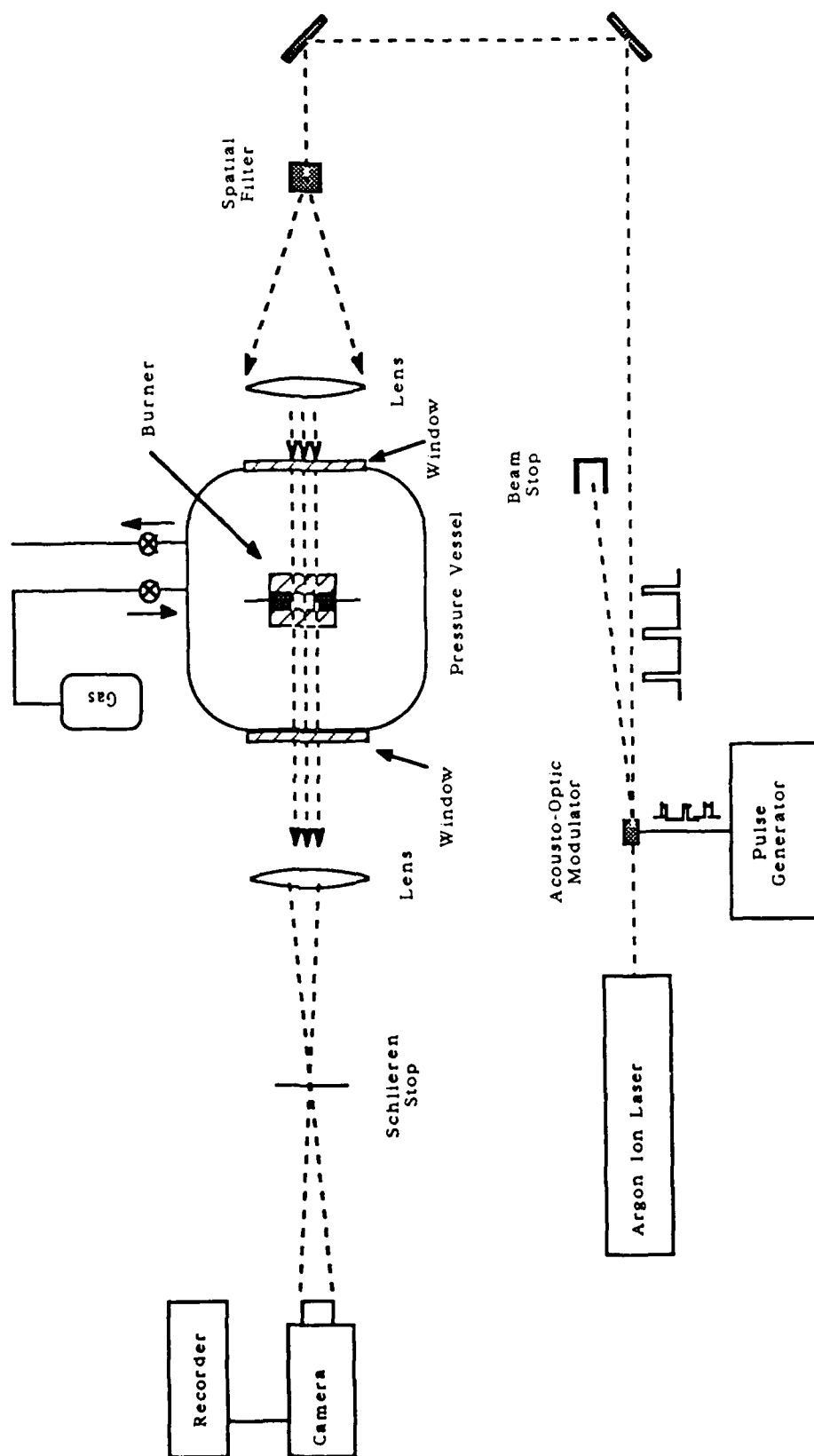


Top view



Side view

# High pressure combustion is photographed



## **LP1846 and HAN-water mixtures have been studied**

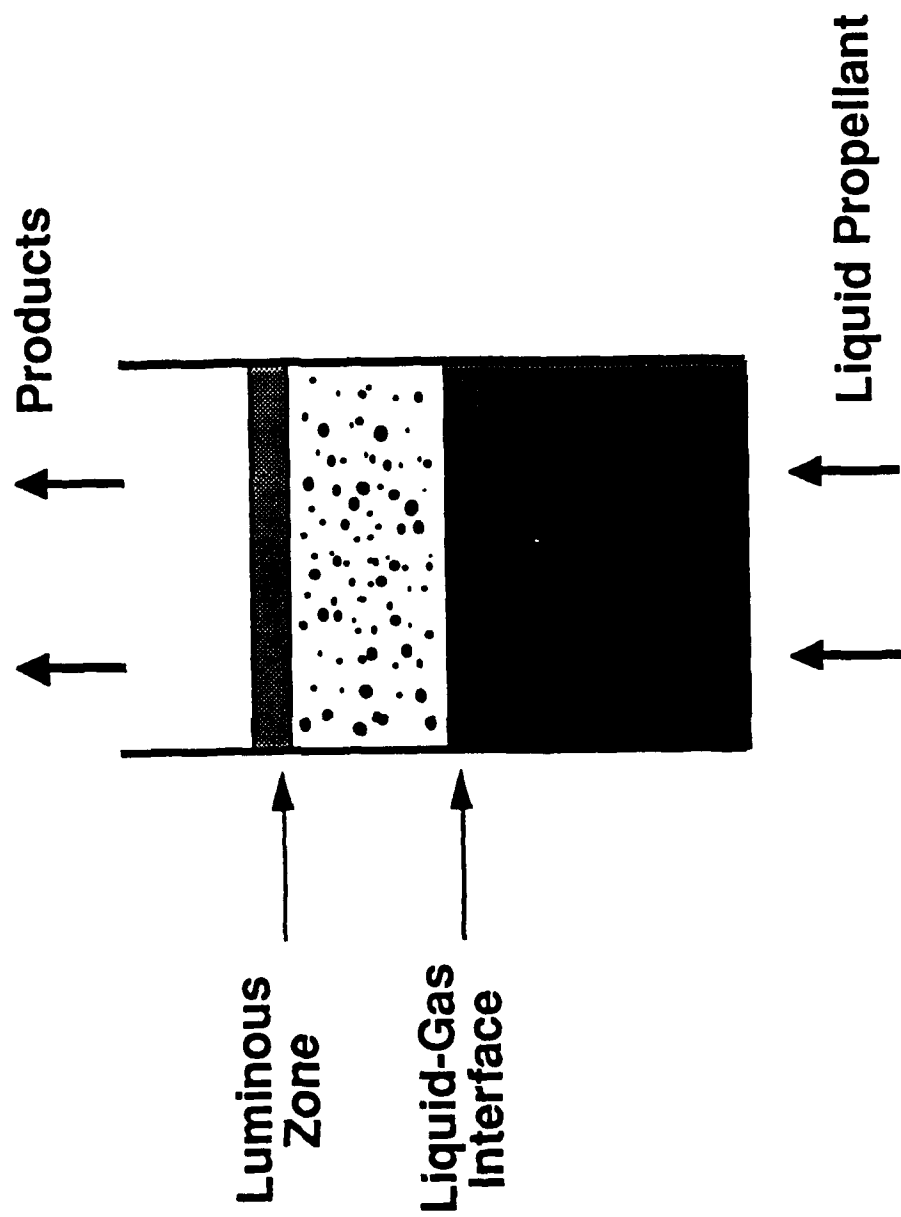
**Propellants: HAN - TEAN - Water (LP1846)  
HAN - Water Mixtures (3 - 13 M HAN)**

**Pressure: 7 to 35 MPa (1 to 5 kpsi)**

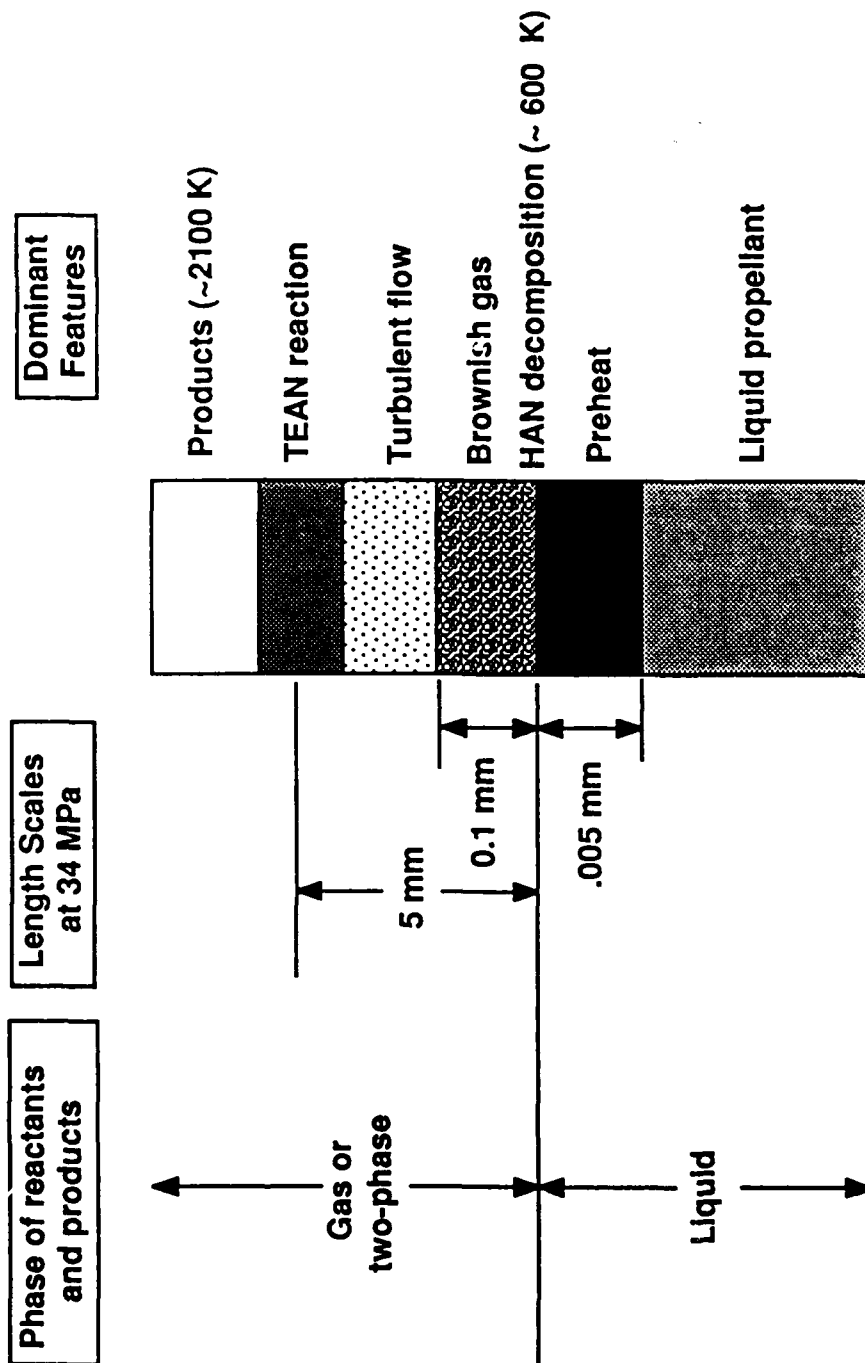
**Temperature: 25 °C**



**LP flame consists of an interface and a luminous zone**



# Liquid propellants have a complex flame structure



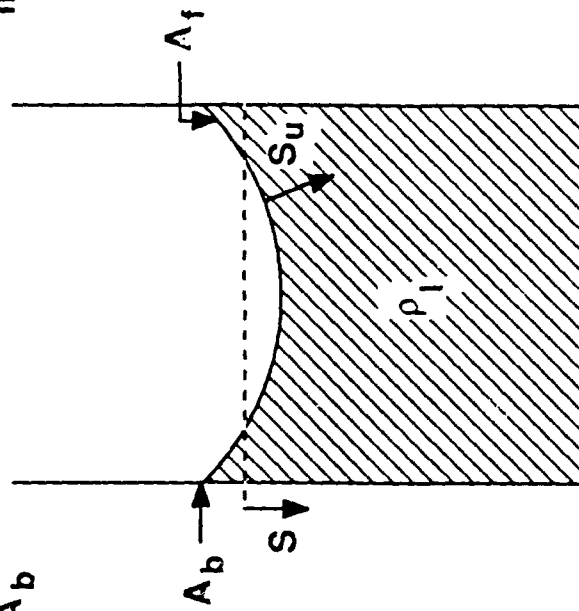
# The mass burning rate depends on the area and burning velocity

"Operational Definition"

$$\dot{m} = \rho_l S A_b$$

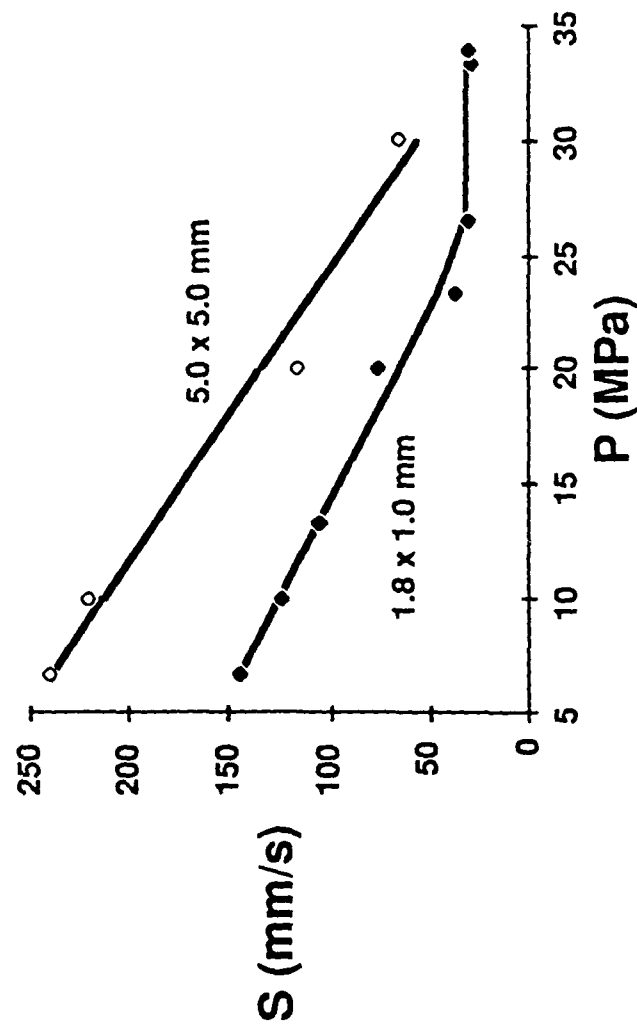
"Fundamental Definition"

$$\dot{m} = \rho_l S_u A_f$$



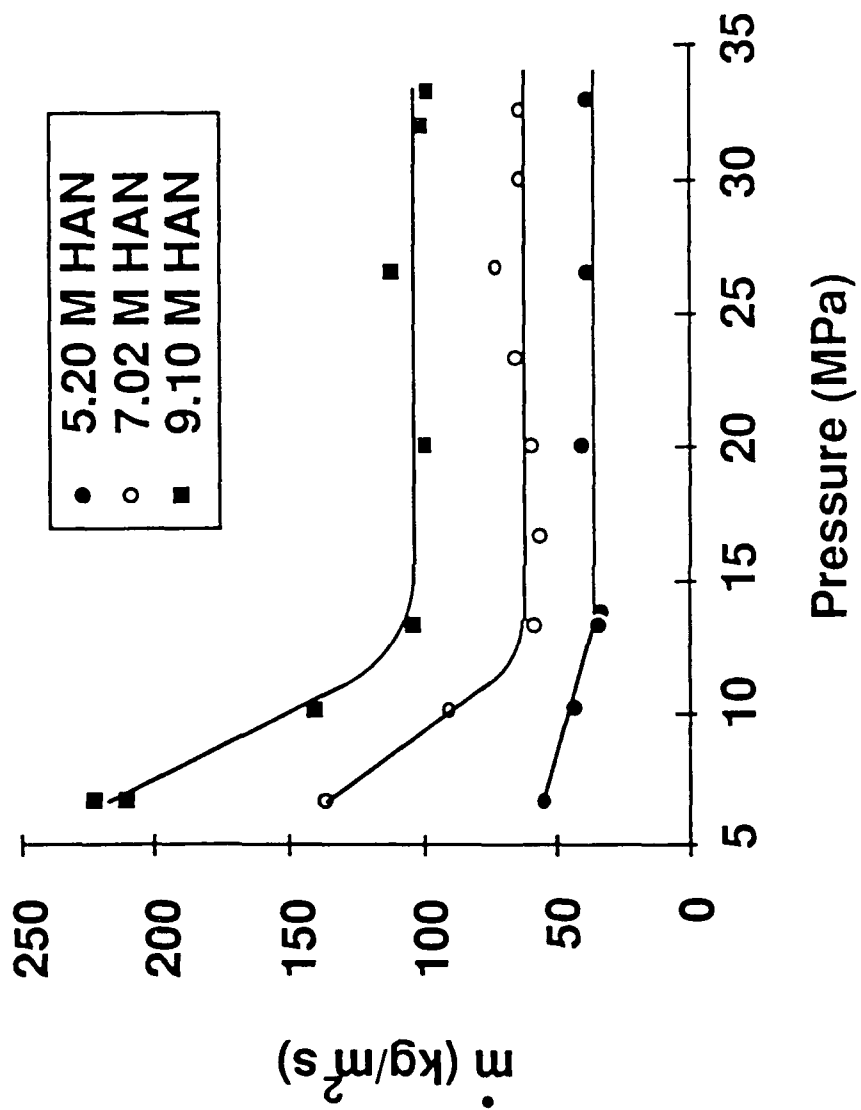
$$\Rightarrow S = S_u A_f / A_b$$

## Burning velocity depends on pressure and burner size

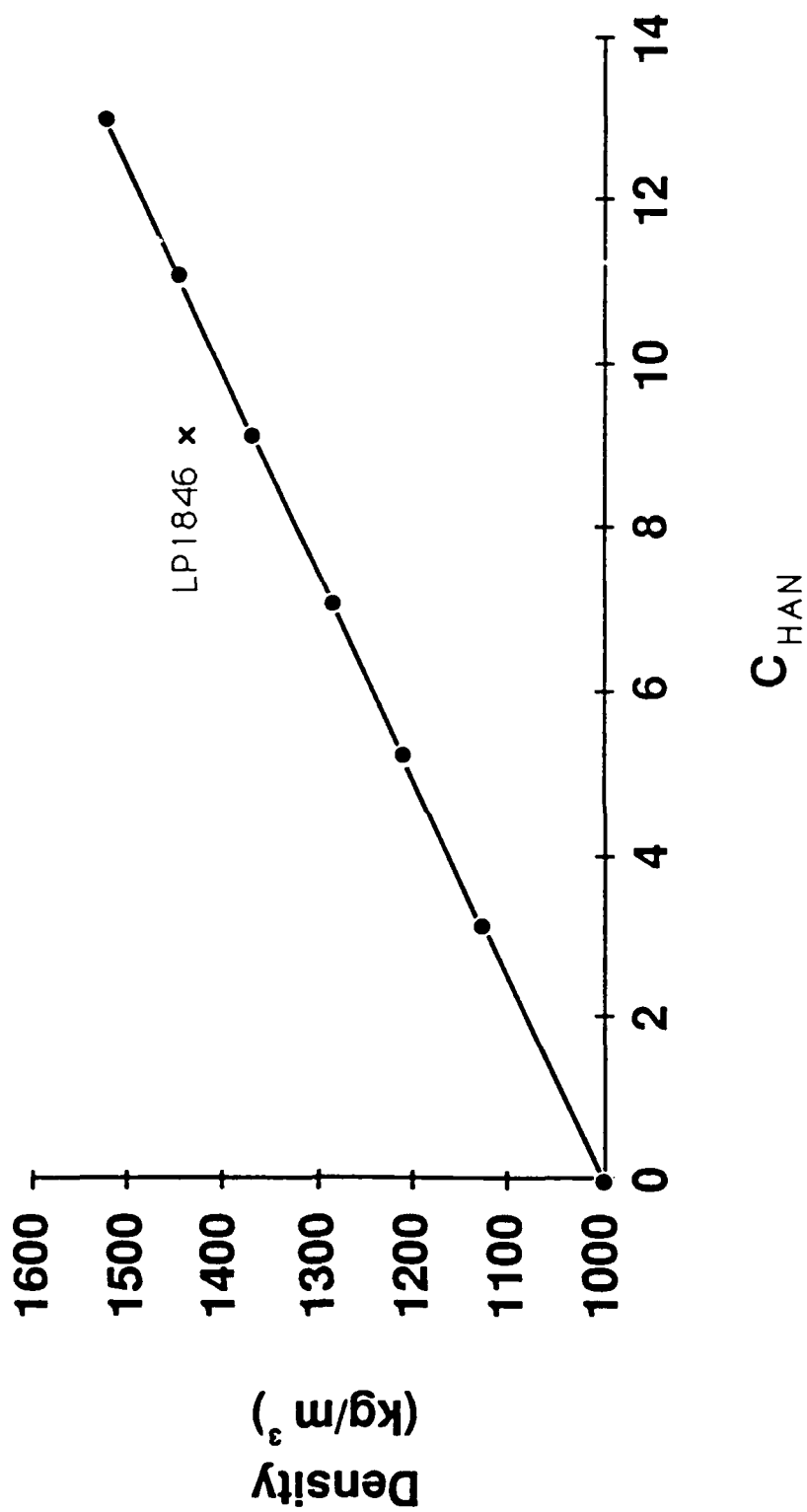


## The pressure dependence changes with pressure

\* Data for a 1.8 x 1.0 mm burner

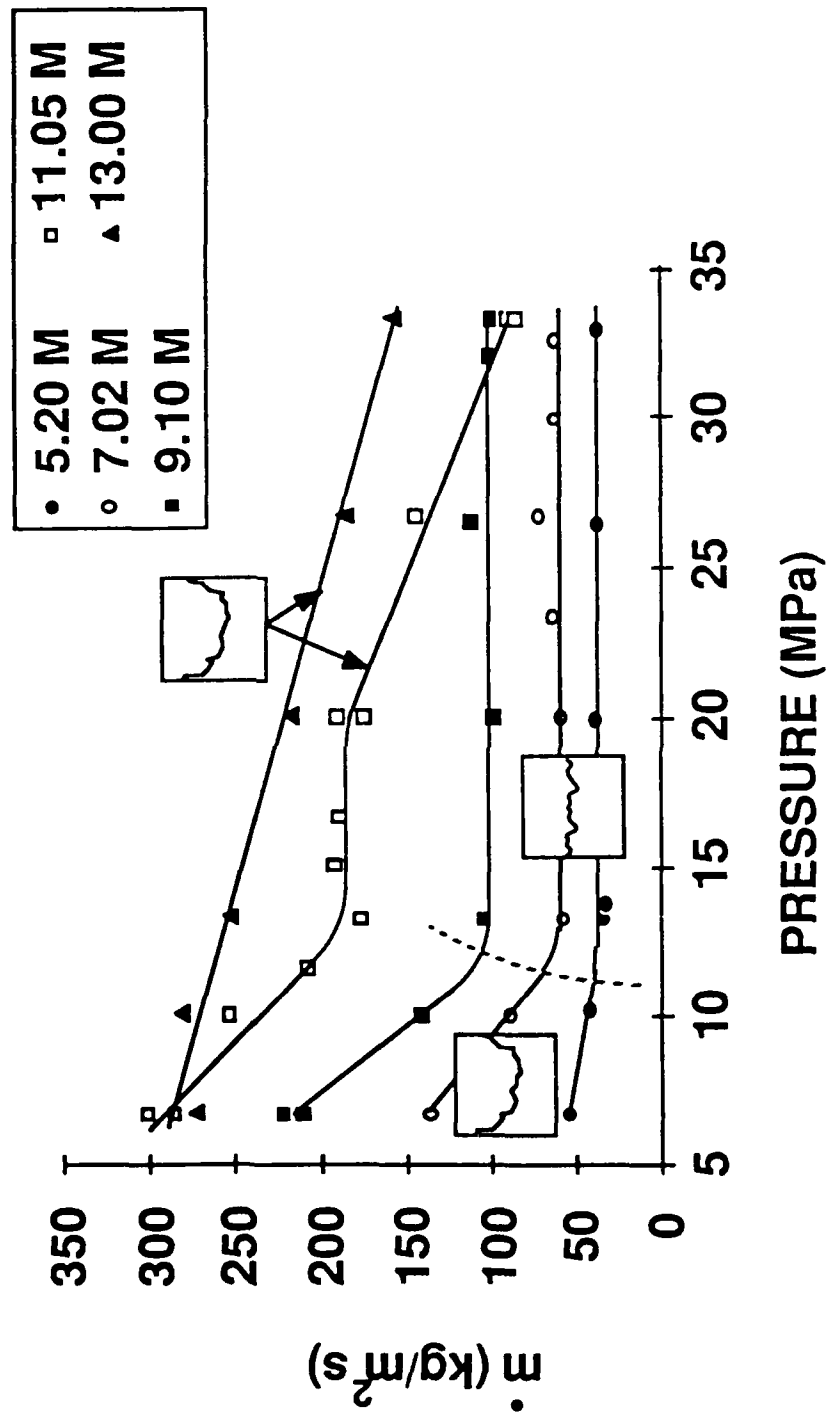


## A range of HAN-water mixtures were studied



## Pressure dependence is related to surface area

\* Data for a 1.8 x 1.0 mm burner

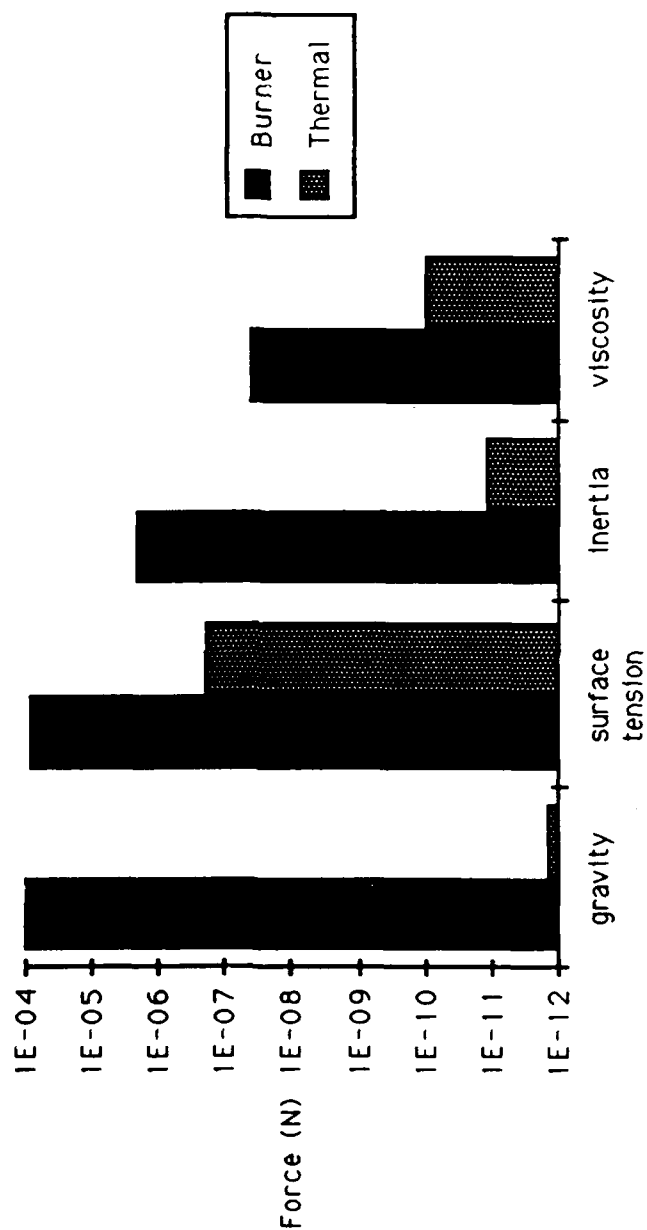


## The stability of the gas-liquid interface is determined by many forces

Force	Magnitude	Burner Size	Estimate Decomposition Zone Thickness
Inertia	$\rho L^2 V^2$	$\rho_u A_b S^2$	$\rho_u \alpha_u^2$
Viscosity	$\mu L V$	$\mu_u A_b^{1/2} S$	$\mu_u \alpha_u$
Surface Tension	$\sigma L$	$\sigma_u A_b^{1/2}$	$\sigma_u \alpha_u / S_u$
Gravity	$g \Delta \rho L^3$	$g \Delta \rho A_b^{3/2}$	$g \Delta \rho (\alpha_u / S_u)^3$



## Gravity, surface tension and inertia forces are dominant



## **A force balance reveals important correlation parameters**

---

The dominant forces on the liquid surface are surface tension, acceleration and inertia.

Important parameter are:

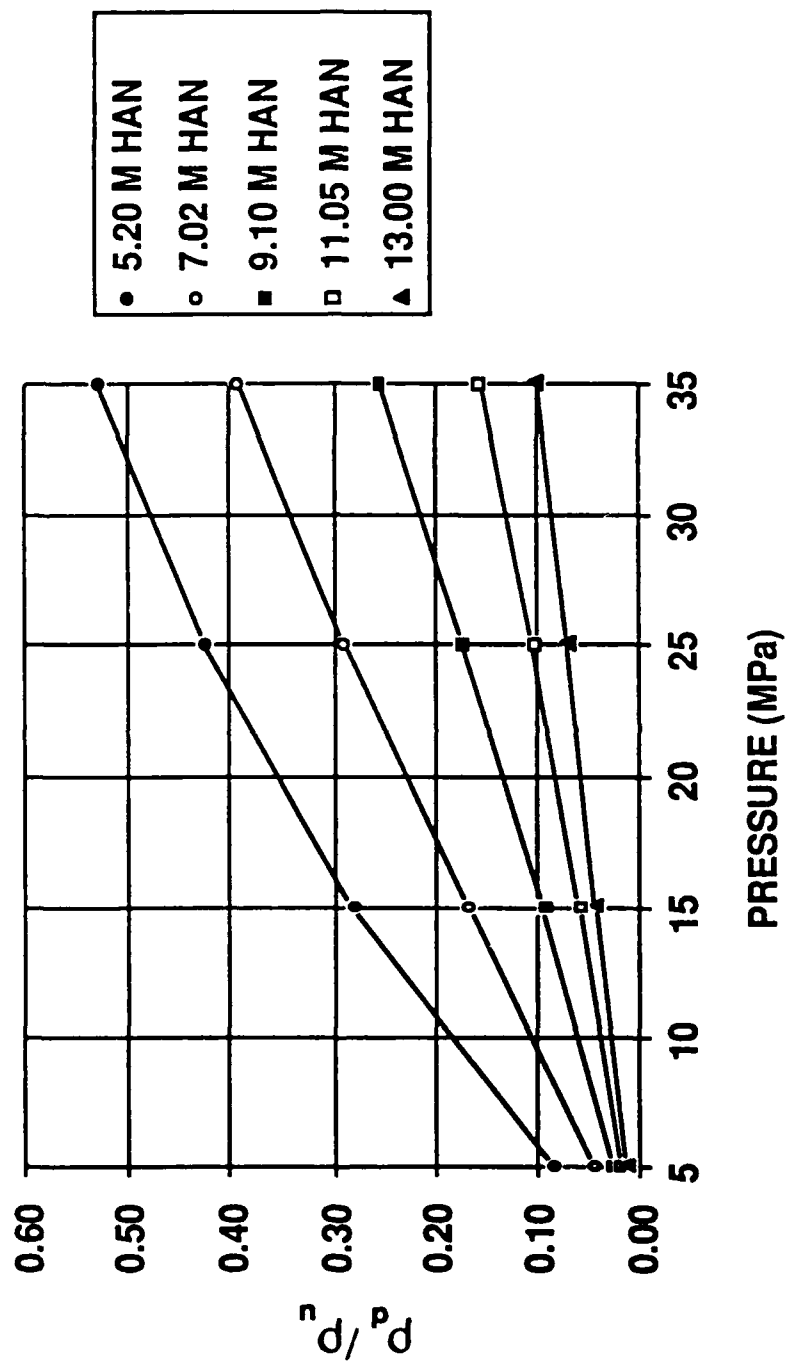
Density ratio across the interface:  $\rho_l / \rho_u$

Surface tension parameter:  $\sigma / g \Delta \rho L^2$

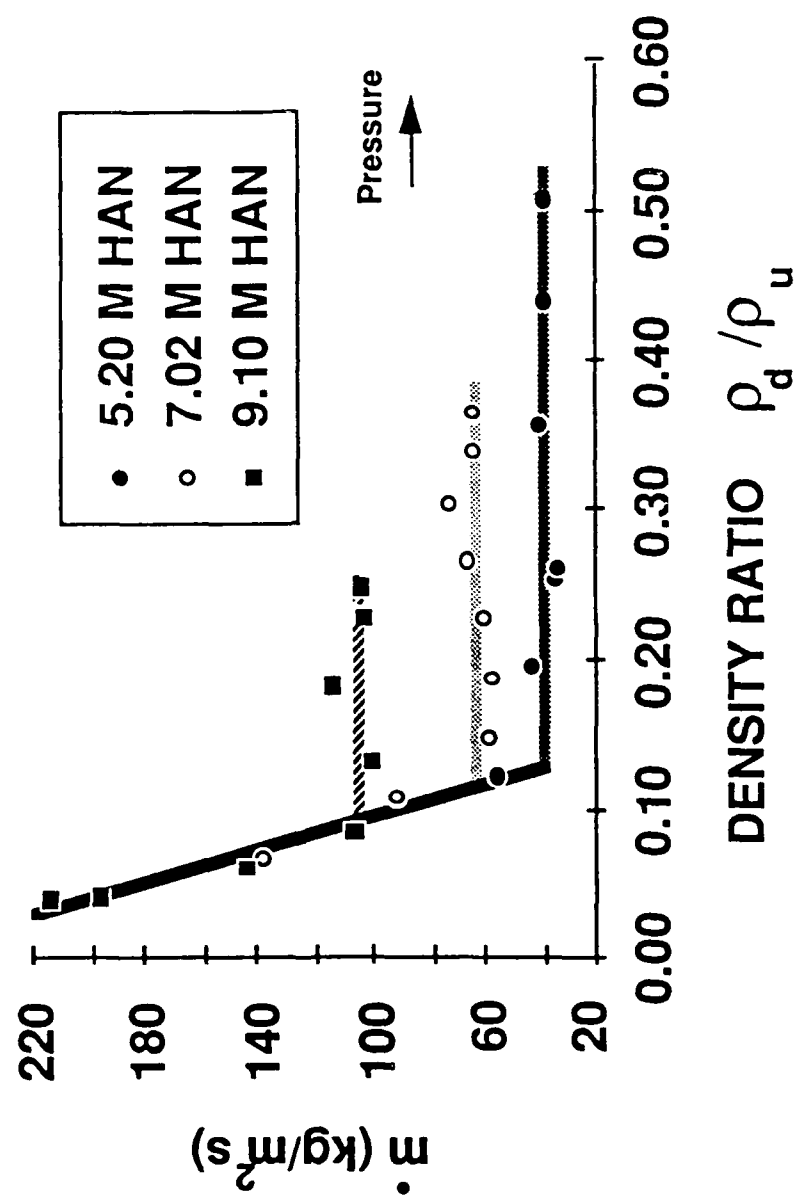
## **Equilibrium calculations give the density ratio**

- Calculate the density ratio across the liquid-gas interface of decomposing HAN-water mixtures.
- Assume that HAN decomposes adiabatically into nitrogen, water, nitric acid and nitrogen dioxide.
- Calculate the decomposition density to correlate the decomposition rate.

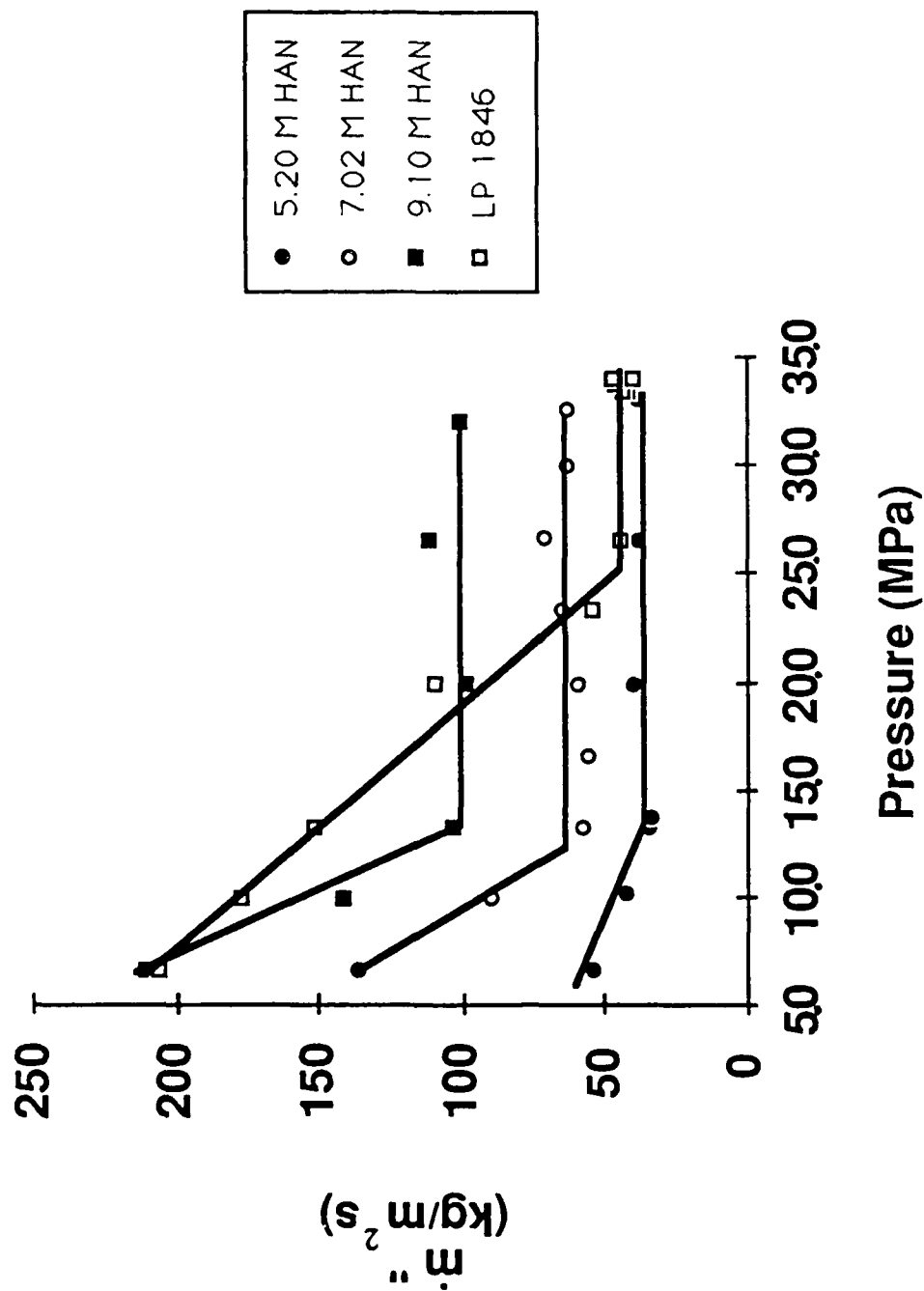
**The density ratio increases with pressure  
and decreases with HAN concentration**



## Decomposition rates correlate with density ratio



# LP1846 burning velocity follows same trend as do HAN-water decomposition rates

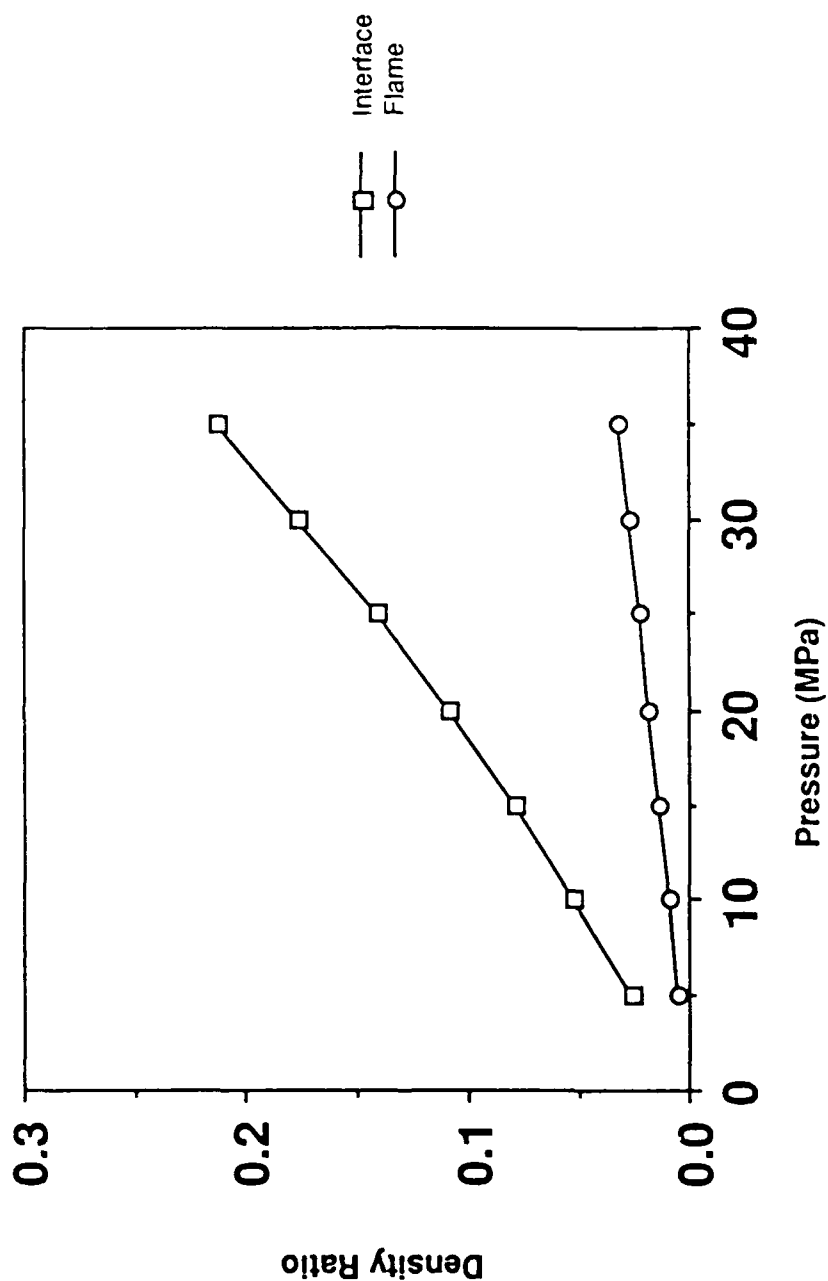


## **The LP gas-liquid interface density ratio estimated from an equilibrium calculation**

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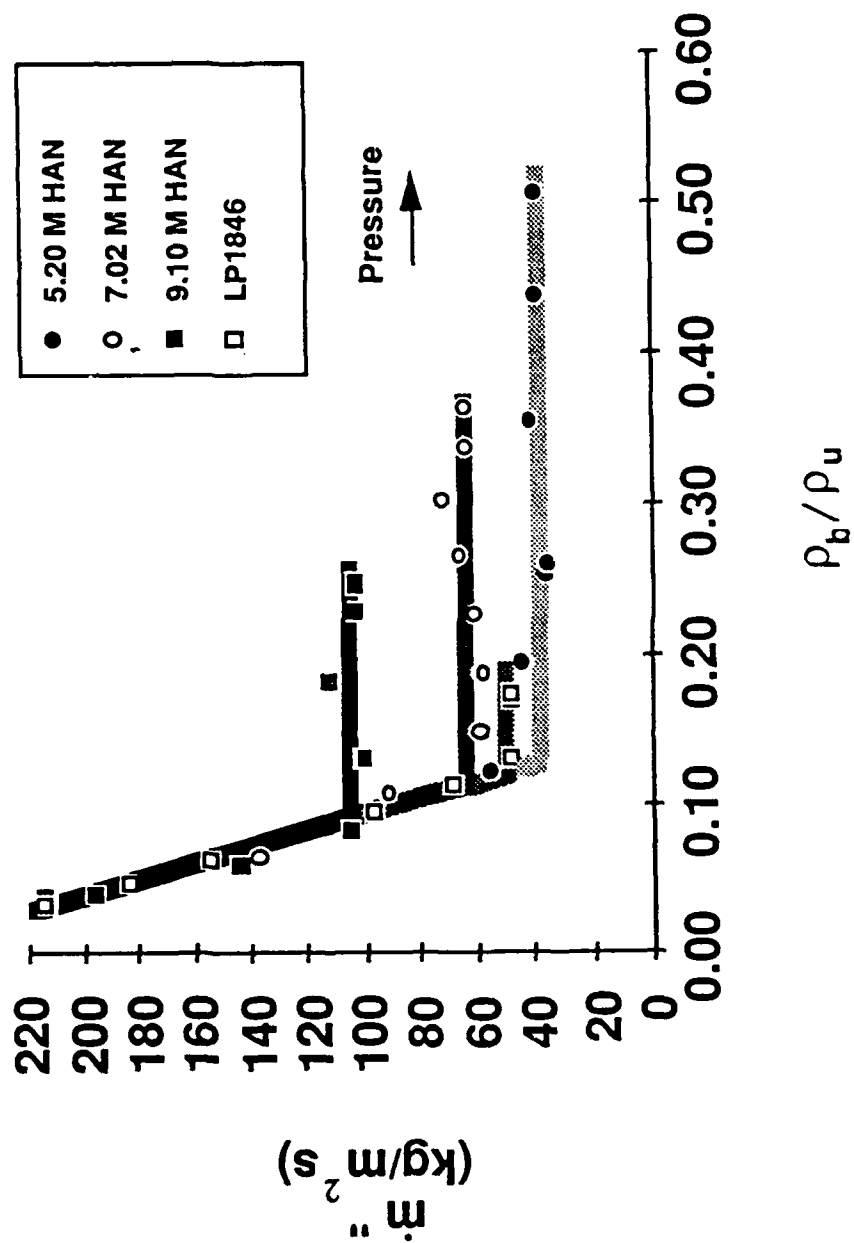
- Calculate the density ratio across the liquid-gas interface of combusting LP1846.
- Assume the interface corresponds to HAN decomposition to nitrogen, water, nitric acid and nitrogen dioxide.

**The LP1846 density ratio is similar to that of HAN-water**

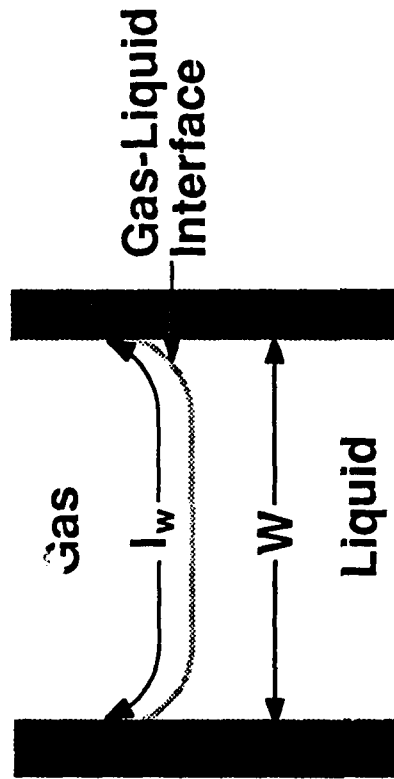




# LP1846 burning velocity correlates with density ratio



The laminar burning velocity is estimated from photographs of nearly planar burning

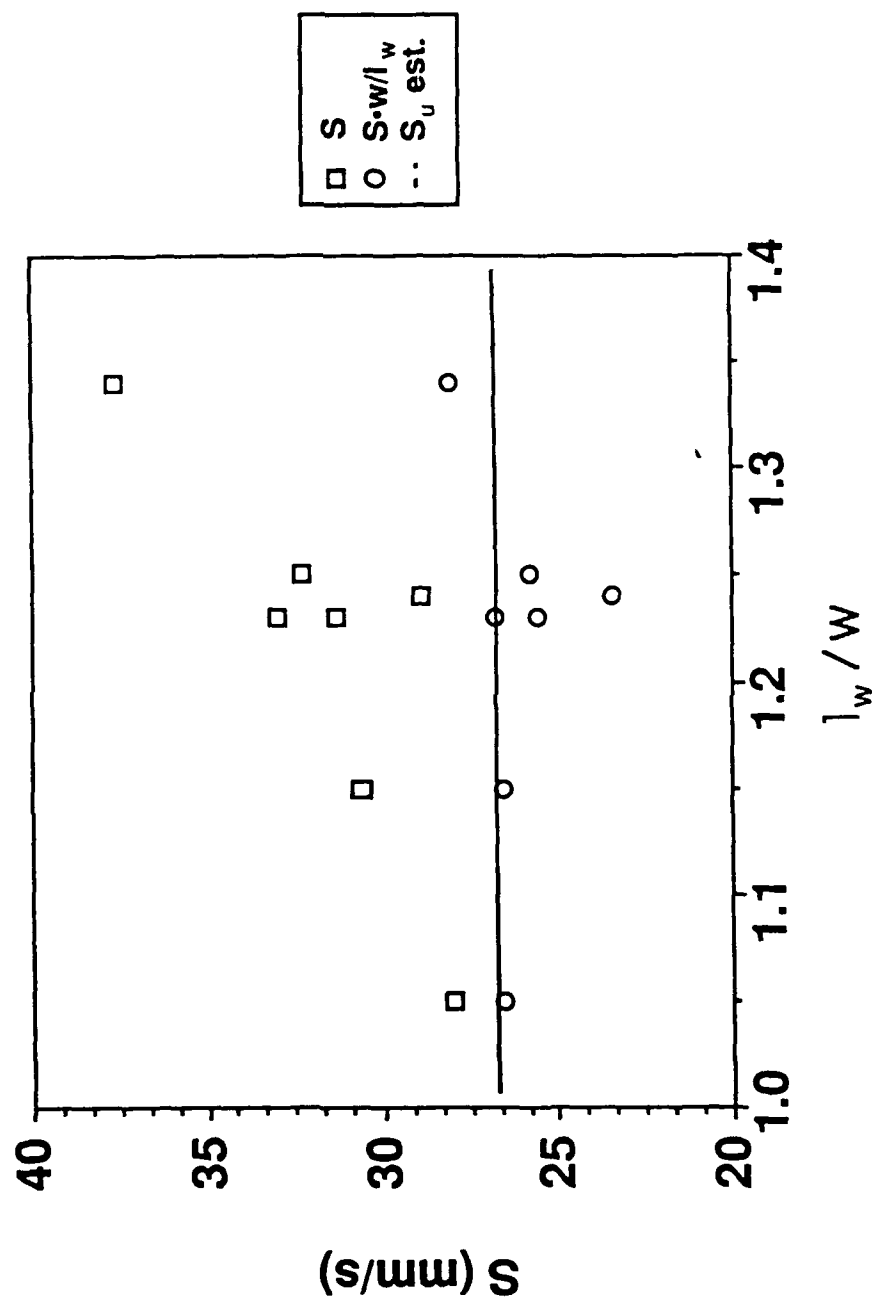


$W$  = Burner width

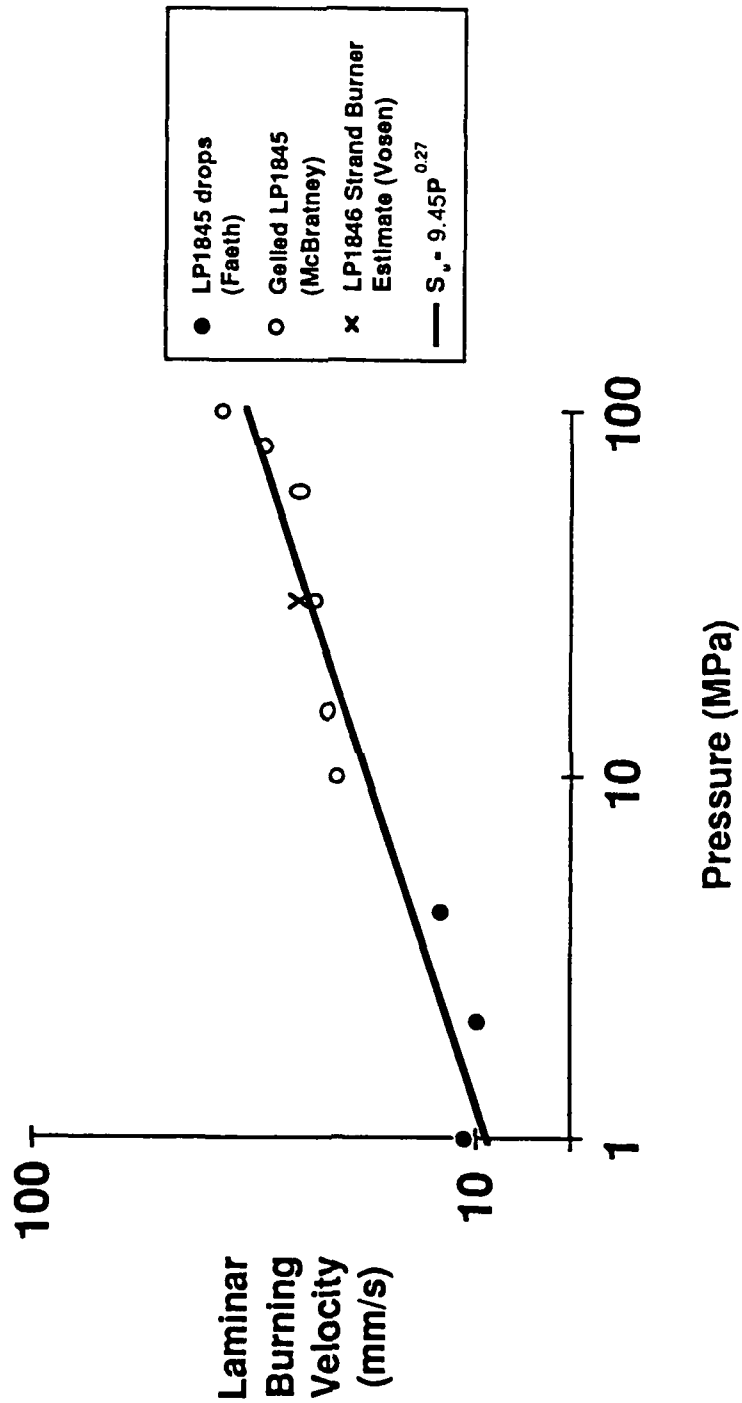
$l_w$  = Interface Length

To first order,  $S_u = S_b / A_l \approx S W / l_w$

The laminar burning velocity is obtained from corrections to the measured burning velocity



# Strand burner velocities agree with other measurements



## **Conclusions**

---

- 1) LP flames consist of HAN decomposition followed by TEAN reaction.
  - a) LP burning velocities are dominated by HAN decomposition.
  - b) Gas phase reactions between liquid surface and TEAN reaction zones have been observed.
- 2) Apparent burning velocities are a combination of:
  - a) a nearly pressure independent laminar burning velocity,
  - b) instabilities are more pronounced for lower pressures and larger burners.

## Conclusions (cont)

- 3) Inverse burning rate pressure dependence results from physical effects (hydrodynamics). The important factors to consider are:
  - a) the density ratio across the gas-liquid interface, and
  - b) the burner geometry
- 4) Hydrodynamic effects can be eliminated for small burners, giving strand burning velocity measurements that agree with those on liquid drops and gelled propellant. For pressures of 1 to 100 MPa the laminar burning velocity is:

$$S_u = 9.45P^{0.275}$$

$S_u$  in mm/s

$P$  in MPa

## **Future Directions**

---

- Thermal and electrical ignition of liquid propellant
  - Study thermal and electro-chemical ignition mechanisms
    - ignition limits, condensed phase reactions
    - thermal ignition (by CO<sub>2</sub> laser) has been demonstrated
- Image processing of LP combustion
  - Identify modes of burning instability
  - use of color image processing to identify gas phase species
  - study liquid jet combustion (Sandia I /C)

5th ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT  
US ARMY BALLISTIC RESEARCH LABORATORY  
ABERDEEN PROVING GROUND, MD  
22-24 AUG 89

Title of Paper Deducing Useful Data From Images of HAN-based Liquid  
Propellant Combustion  
Presentation Time Request 20 (min)  
Type of Paper: Progress; Summary; X State-of-art; Other  
Speaker's Name R. C. Armstrong Phone Number (415) 294-2470  
Affiliation/address Sandia National Laboratories  
Livermore, CA 94551-0969  
Co-author(s) name(s) S. R. Vosen

ABSTRACT (Use reverse side if necessary)

At experimental conditions relevant to gun applications, HAN-based liquid propellants present enormous difficulties in experimental diagnostics. Fortunately the unburned and burned states are optically clear, providing for an attractive environment for high-speed cinematography, although the experimental difficulties are still great. The analysis of the resulting film for quantitative information is problematic and, as yet, largely untried. First, as with all photographic/video data, there is an enormous amount of it, only a small part of which is desired. In our case we wish to track and quantify the unstable, combustng gas/liquid interface in strand burning experiments of LP and render it as a one-dimensional line embedded in a two-dimensional plane. We found existing edge enhancement techniques inadequate, and developed our own algorithms for extracting this line. Thus we obtain a translating and deforming gas/liquid interface for each frame in time. These are spaced closely enough that the interface can be considered continuous. Second, it must be realized that the photograph is actually a two-dimensional projection of a three-dimensional reality. We have dealt with this by considering the gas/liquid interface to be a stochastic process, and used the statistics of extrema to calculate useful results such as the expectation of the frontal area presented by the gas/liquid interface to the flame. From the area estimates of the "real" or "intrinsic" burning rate can be obtained. Extensions to this work regarding more complicated one- and two-phase combustng flows are also of interest. A particularly promising technique for analyzing such flows is linear response theory generalized from (molecular) light and neutron scattering applications.

† This work is supported by the Department of Defense through a Memorandum of Understanding with the Department of Energy and Sandia National Laboratories.

ABSTRACT DEADLINE: JUNE 15, 1989



GAS DRIVEN LP INJECTOR/COMBUSTOR  
DESIGN, TEST OBJECTIVES AND PRELIMINARY TESTS

RAY RYCHNOVSKY  
SANDIA NATIONAL LABORATORIES  
LIVERMORE, CALIFORNIA

PRESENTED AT

FIFTH ANNUAL CONFERENCE ON  
HAN-BASED LIQUID PROPELLANTS

AUGUST 22, 1989

BALLISTICS RESEARCH LABORATORY  
ABERDEEN, MD

Gas Driven LP Injector/Combustor Tester--  
Design, Test Objectives and Preliminary Tests

Ray Rychnovsky  
Sandia National Laboratories  
Livermore, California

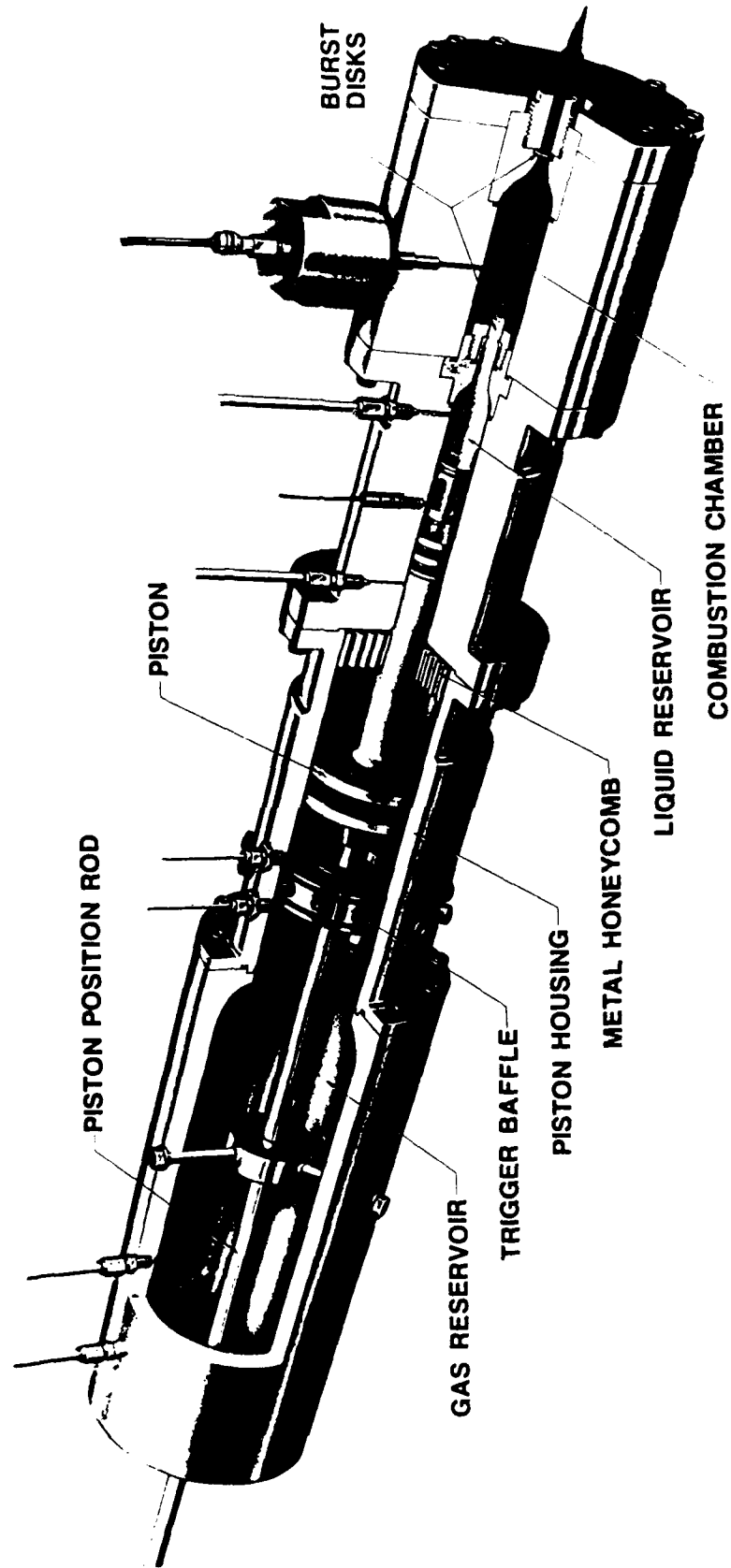
We have designed an injector/combustor to study fundamentals of Liquid Propellant combustion at pressures typical of 155 mm guns. The initial tests will focus on instabilities of combustion. Parameters of injection, jet break up and burning of the LP which will improve mathematical modeling of LP combustion will be measured.

The test apparatus is a gas driven injector/combustor which has a fixed geometry combustion chamber with an exit orifice that is varied to maintain the desired combustion parameters. The liquid propellant chamber is designed for pressures up to 380 Mpa (55 ksi) and the combustion chamber may reach peak pressures of 345 Mpa (50 ksi). Both circular and annular LP injection orifices have been designed and procured.

Tests to date have demonstrated injection parameters and have developed a relatively smooth pressure vs time profile in the LP chamber. Combustion tests will begin soon. The paper will describe the test setup and test results.

This work is jointly supported by the DOD Office of Munitions and by the Department of Energy through a Memorandum of Understanding.

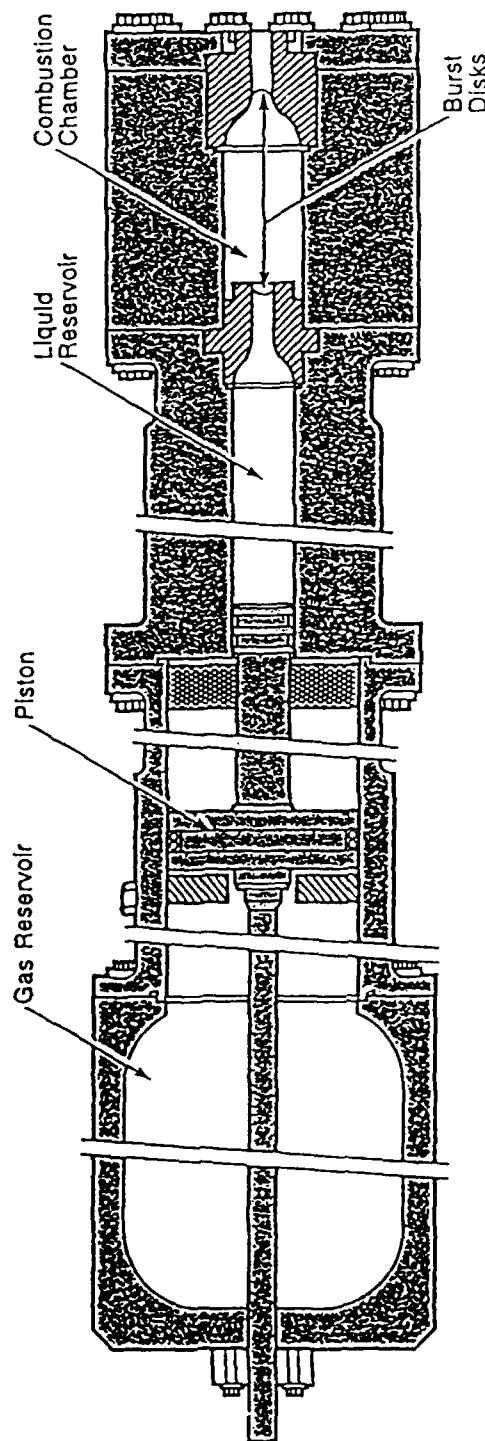
# LP INJECTOR/COMBUSTOR



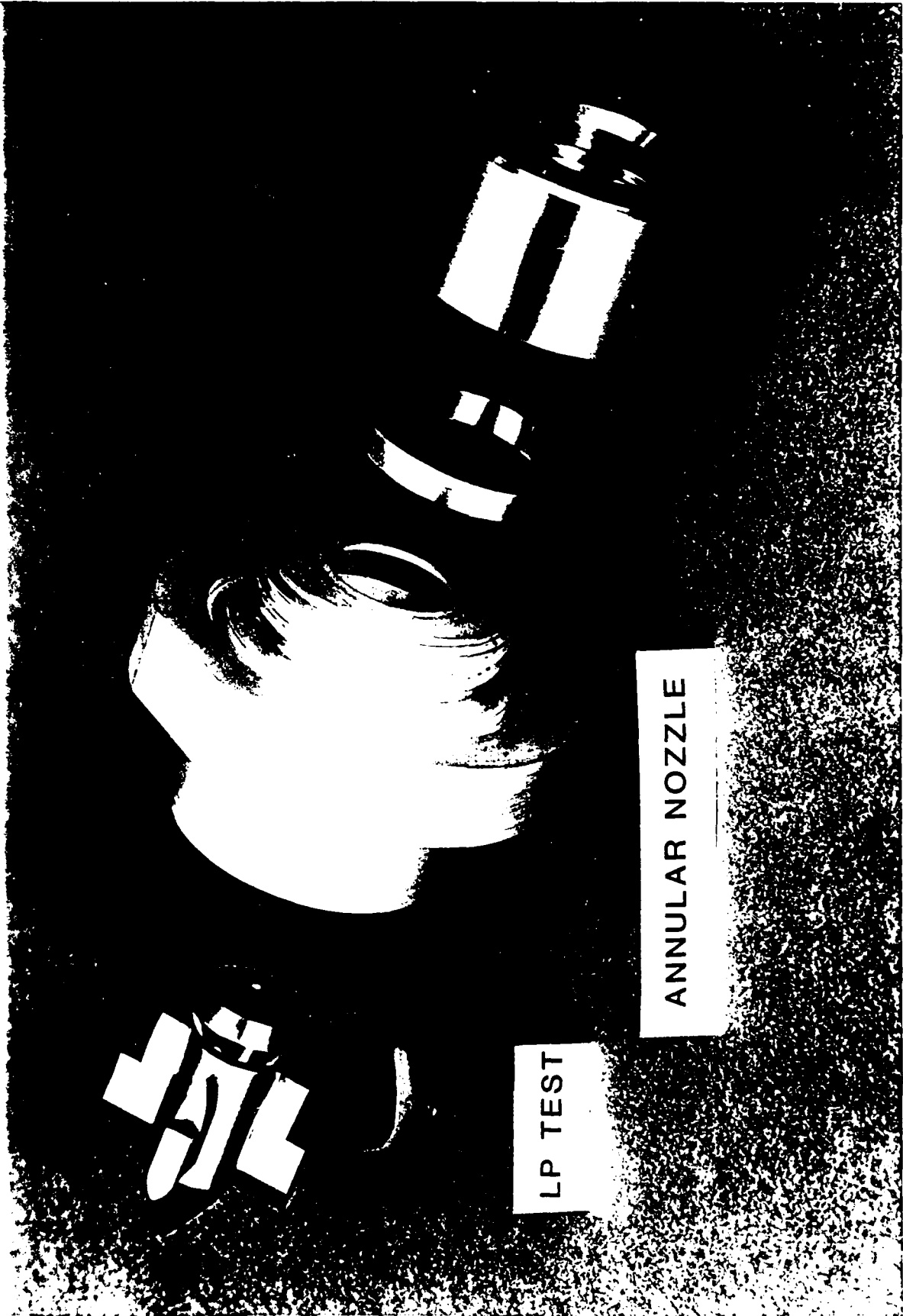
SL-22545A



## The LP I/C was designed to meet specific criteria



- 50,000 psi in combustion chamber
- LP velocity of 50 lbs/s
- test time of 5 to 10 msec
- state-of-the-art diagnostics
- flexibility in design and use

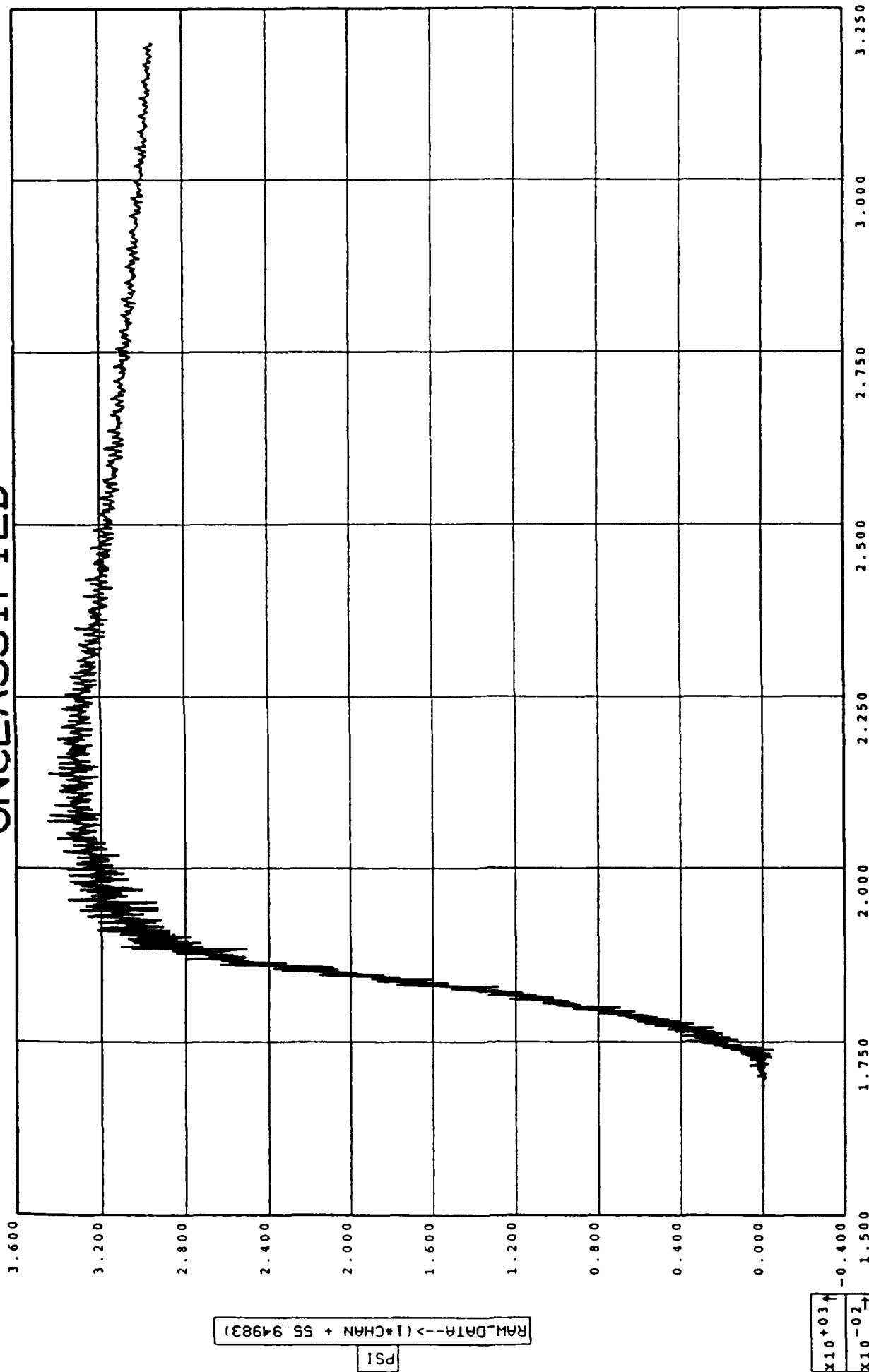


LP INJECTION/COMBUSTION TESTS COMPLETED - 8/16/89

TEST NO	TEST DATE	CHARGE			PRESS-KSI		RUPT. DISC STRENGTH		ORIF	CC PRESS H/C		
		IGNITER	MAIN		HE	LP	LP	CC		KSI	ksi	
		4350 GMS	LP CC	LP CC	ksi	ksi	ksi	ksi				
WATER EJECTION TESTS												
WE - 1	3/17	-	-	-	0.50	1.7	3.0	-	5 mm	-	1.0	
WE - 2	3/23	-	-	-	0.55	1.7	3.0	-	5 mm	-	1.0	
WE - 3	4/13	-	-	-	1.00	3.8	6.0	-	5 mm	-	1.0	
WE - 4	4/14	-	-	-	1.00	4.0	6.0	-	5 mm	-	1.0	
WE - 5	4/14	-	-	-	1.00	4.5	6.0	-	5 mm	-	1.0	
WE - 6	4/21	-	-	-	1.00	3.7	6.0	-	8 mm	-	1.0	
WE - 7	4/26	-	-	-	1.00	4.0	6.0	-	8 mm	-	1.0	
WE - 8	5/3	-	-	-	1.00	3.9	6.0	-	8 mm	-	1.0	
WE - 9	5/4	-	-	-	1.30	2.9	10.0	-	8 mm	-	1.0	
WE -10	5/10	-	-	-	1.30	2.5	10.0	-	8 mm	-	1.0	
WE -11	7/7	-	-	-	3.00	4.0	10.0	6.0	5 mm	3.0	3.0	
WE -12	7/12	-	-	-	3.00	4.0	10.0	6.0	5 mm	3.0	3.0	
IGNITION TESTS												
IT - 1		3.5	0	-	-	-	-	-	-	-	-	
IT - 2		2.5	0	-	-	-	-	-	-	-	-	
IT - 3		3.5	0	-	-	-	-	-	-	-	-	
IT - 4		3.5	4	-	-	-	-	-	-	-	-	
IT - 5		3.5	6	-	-	-	-	-	-	-	-	
COMBUSTION TESTS												
CT - 1	7/28	3.5	5	35	3.00	3.6	10.0	6.0	5 mm	0.0	5.0	
CT - 2	8/11	3.5	4	35	3.00	3.6	10.0	6.0	5 mm	0.0	3.0	
CT - 3	8/16	3.5	4	35	3.00	4.0	10.0	6.0	5 mm	0.0	3.0	

MET OBJECTIVE  
OF  
COMBUSTION TEST IN JULY

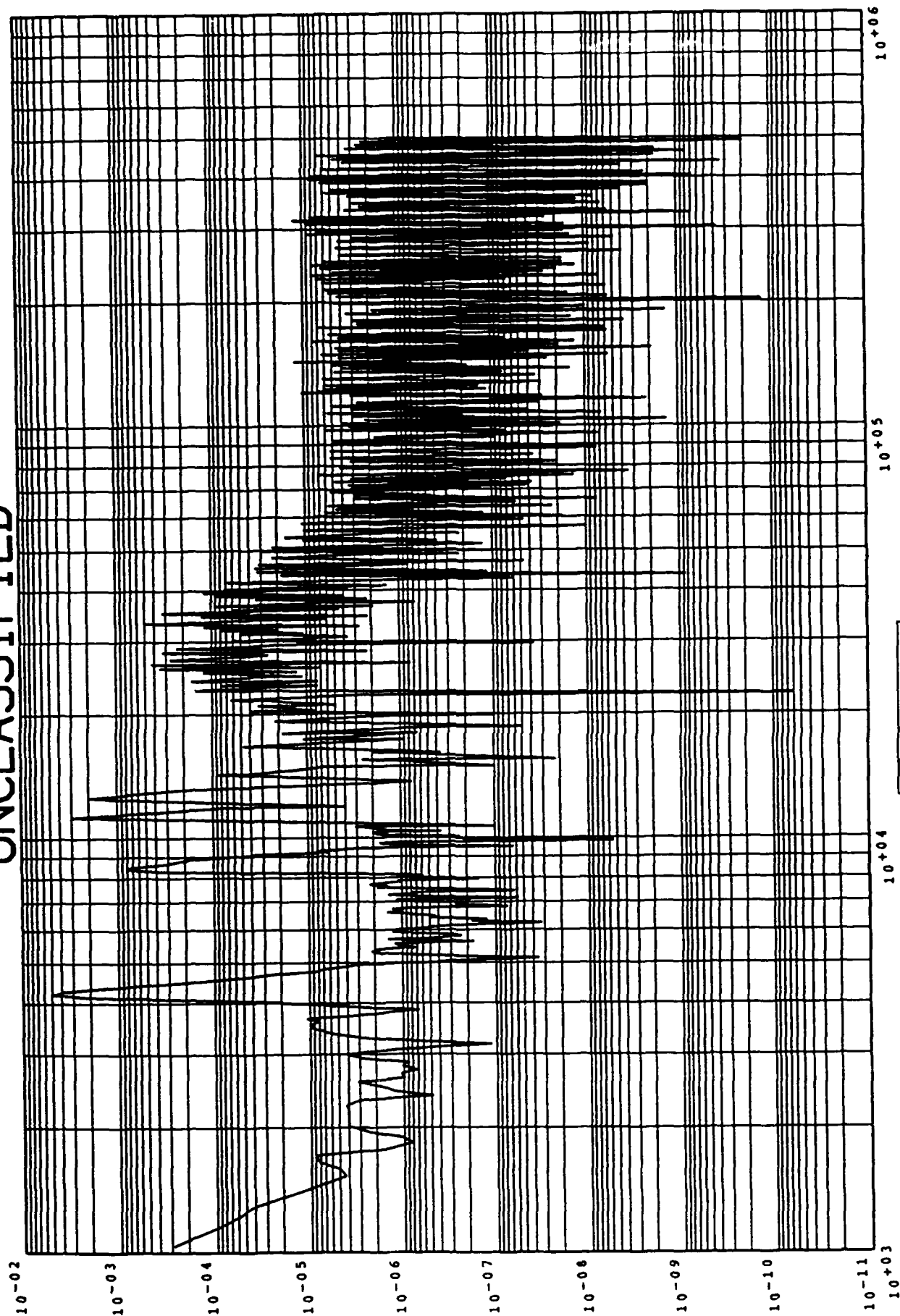
UNCLASSIFIED



206nlr3\_000\_00 89/07/19 18:05:58 LR3 w/3.5 grams 453 + 4cc LP 11-680 LPG IGNITER TESTS  
ID C. 1 2060LR3 Catalyst LPG 1000000 samples/sec CTLYST +  
Data\_Seconds = <0.016799 to 0.032 of 0.131072>

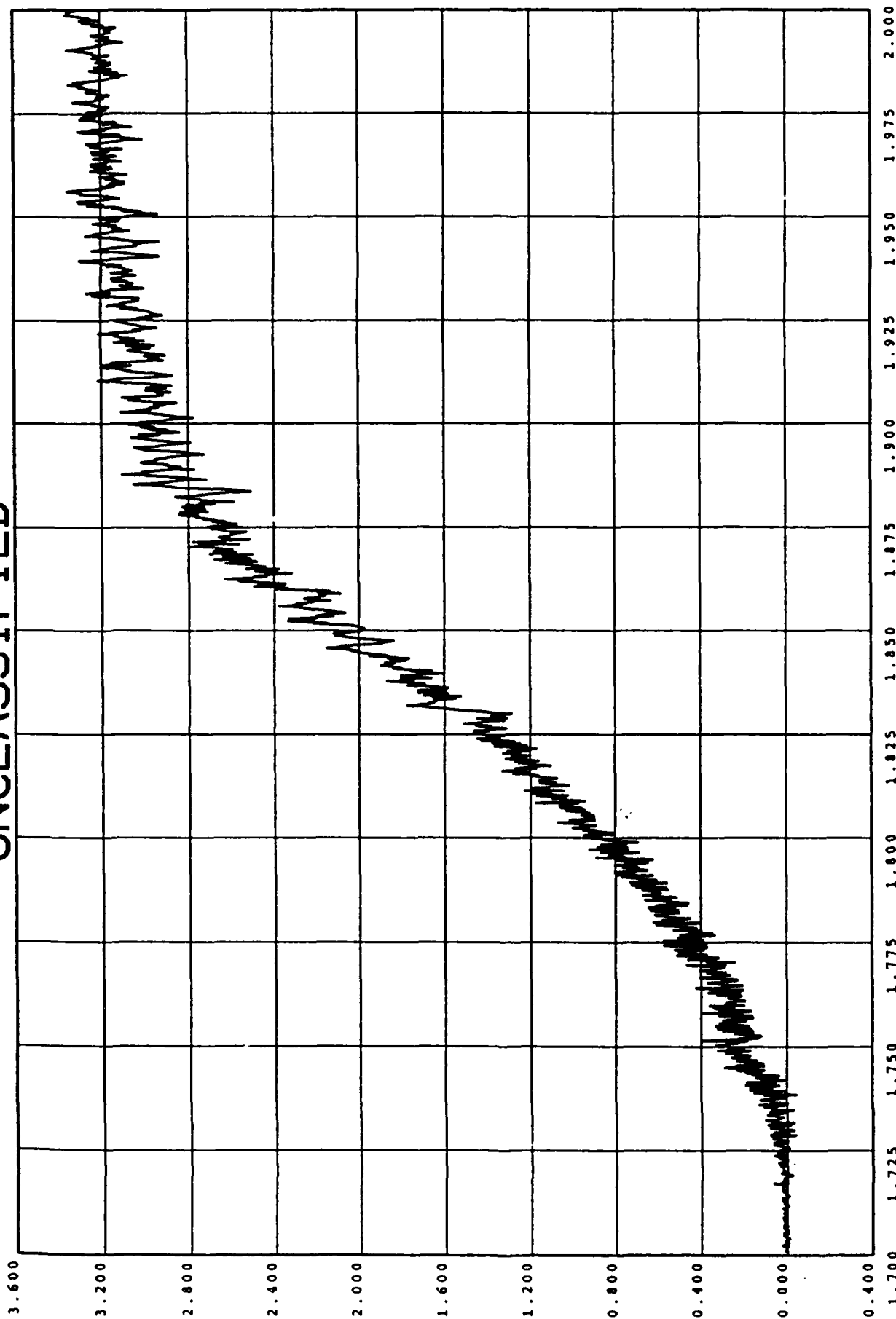


# UNCLASSIFIED



206nlr3\_000\_00 89/07/19 18:05:58 LR3 w/3.5 grams 453 + 4cc LP  
ID C. 1 2060LR3 Catalyst  
Data\_Seconds=(0.016799 to 0.032001 of 0.131072) FFT\_Delta\_Freq = 61.03516 HZ  
Steady State: (Hanning Windowed)

# UNCLASSIFIED



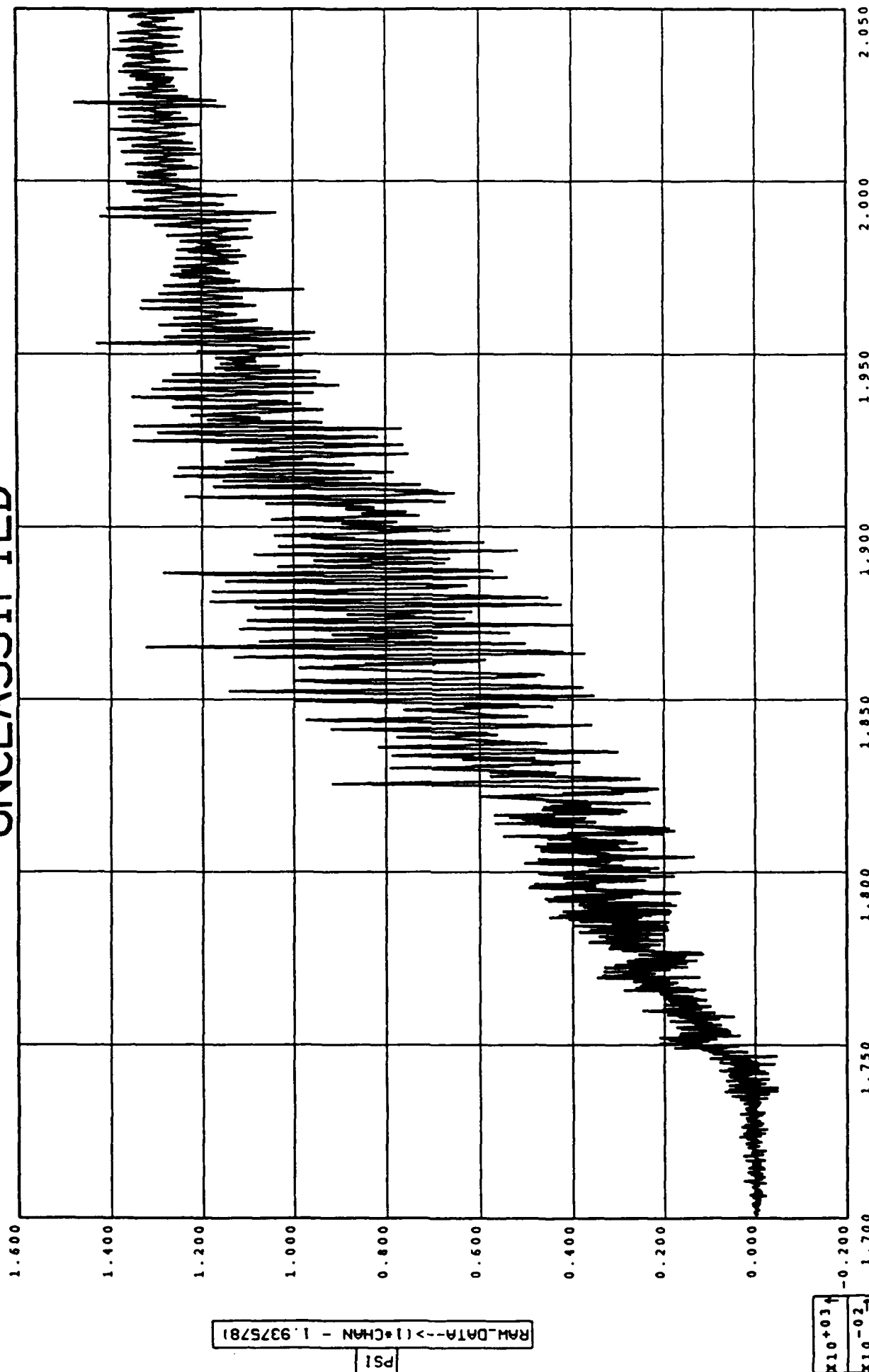
RAW DATA--> (1\*CHAN + 55.94983)

PSI

X10+03  
X10-02

206nlr3\_000\_00 89/07/19 18:05:58 LR3 w/3.5 grams 453 + 4cc LP 11-680 LPG IGNITER TESTS  
 ID C. I 2060LR3 Catalyst LPG 1000000 samples/sec CTLIST +  
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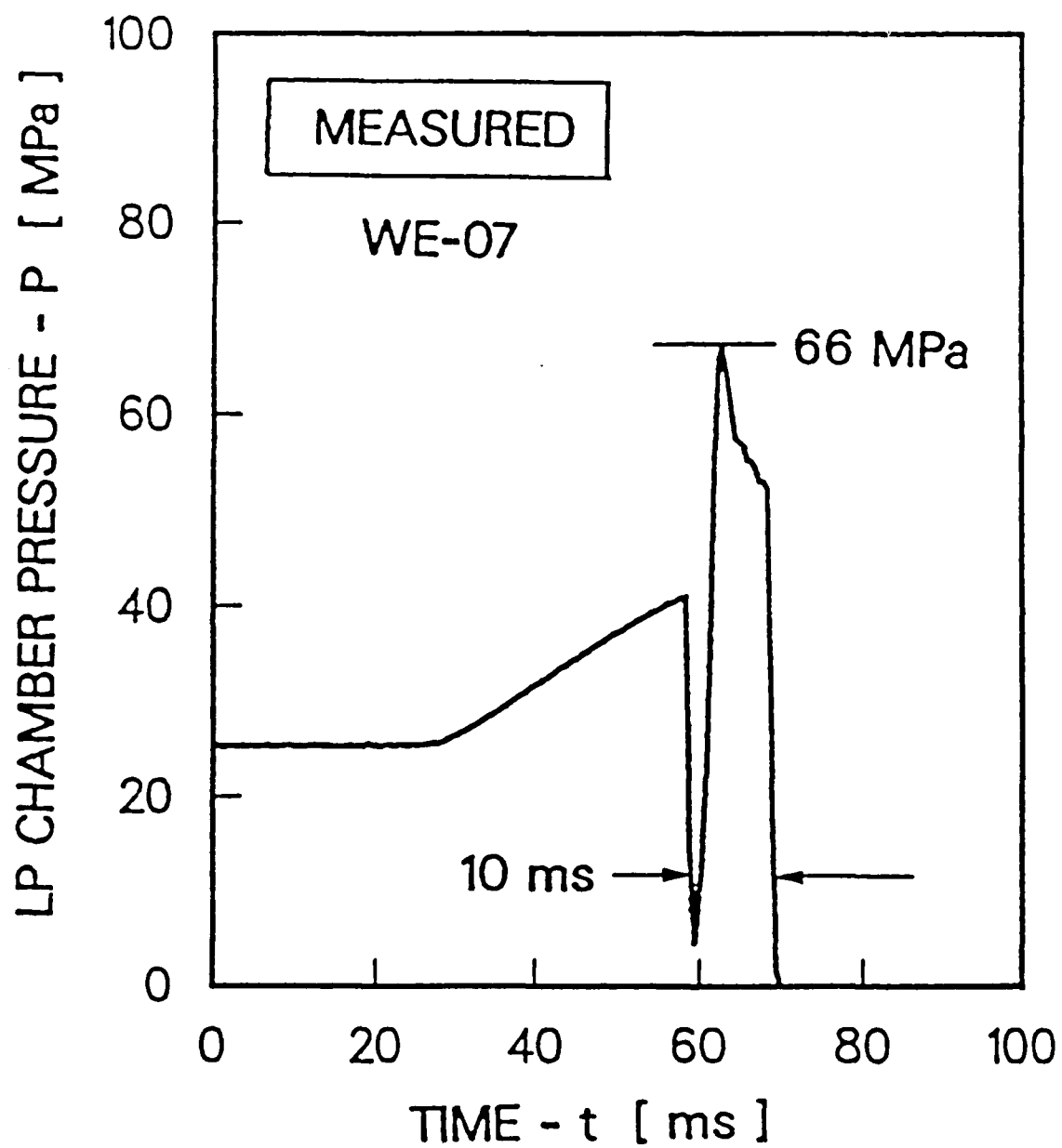
# UNCLASSIFIED



206nr2\_000\_00 89/07/19 12:51:52 LR2 w/3.5 grams 453 11-680 LPG IGNITER TESTS

ID\_C. 1 2060LR2 Catalyst LPG 1000000 samples/sec CTLYST +

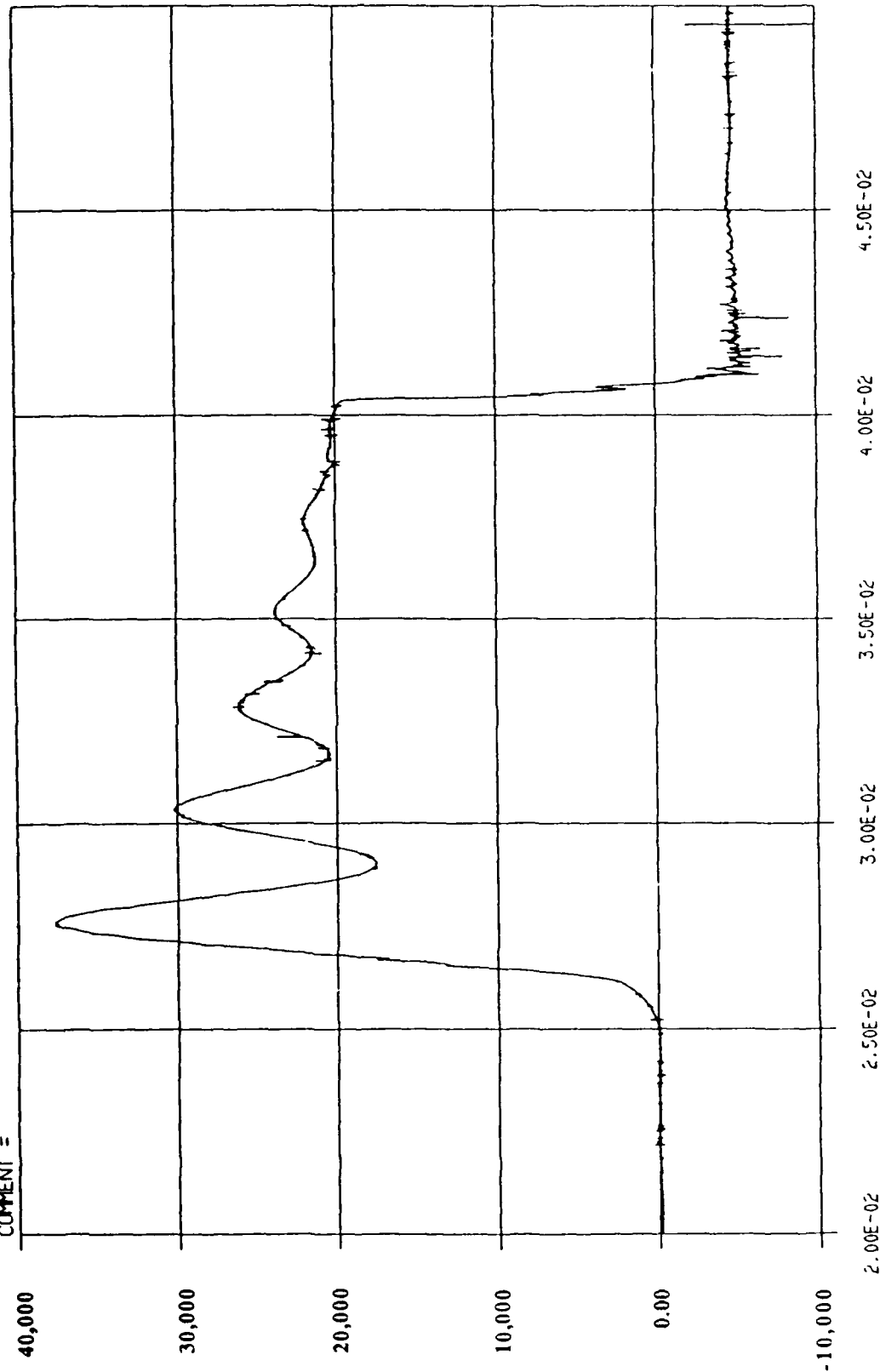
Data\_Seconds = <0.017009 to 0.0205 of 0.131072>



# WE-12

P21.LR1

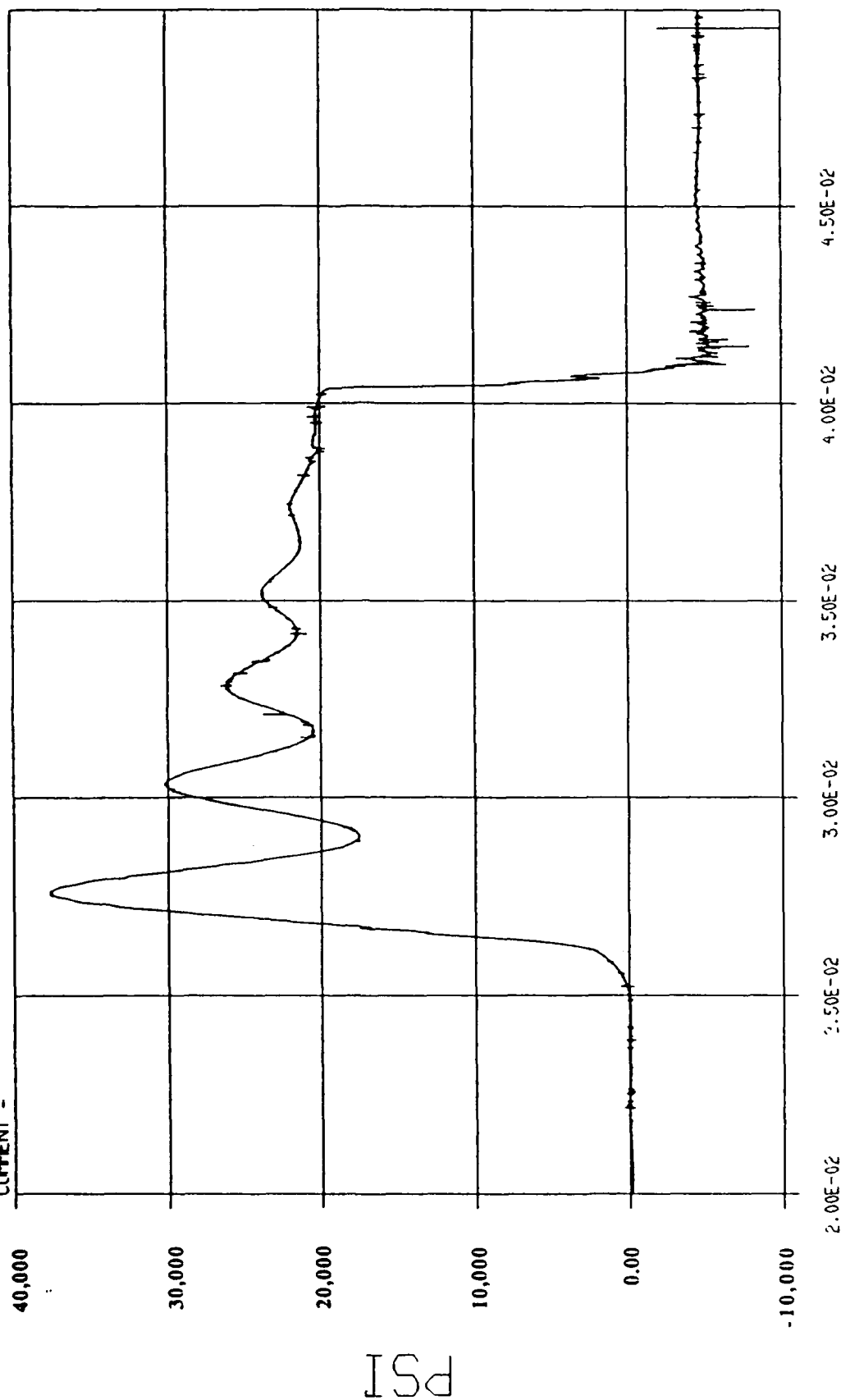
START SAMPLE = 20000  
ENDING SAMPLE = 50000  
# OF SAMPLES = 30001  
SAMPLE INTERVAL = 0.0000E+00  
CAL FACTOR = (PSI /VOLT) = 0.0000  
COMMENT =



# WE-12

START SAMPLE = 20000  
ENDING SAMPLE = 50000  
# OF SAMPLES = 30001  
SAMPLE INTERVAL = 0.0000E+00  
CAL FACTOR = (PSI /VOLT) = 0.0000  
COMMENT =

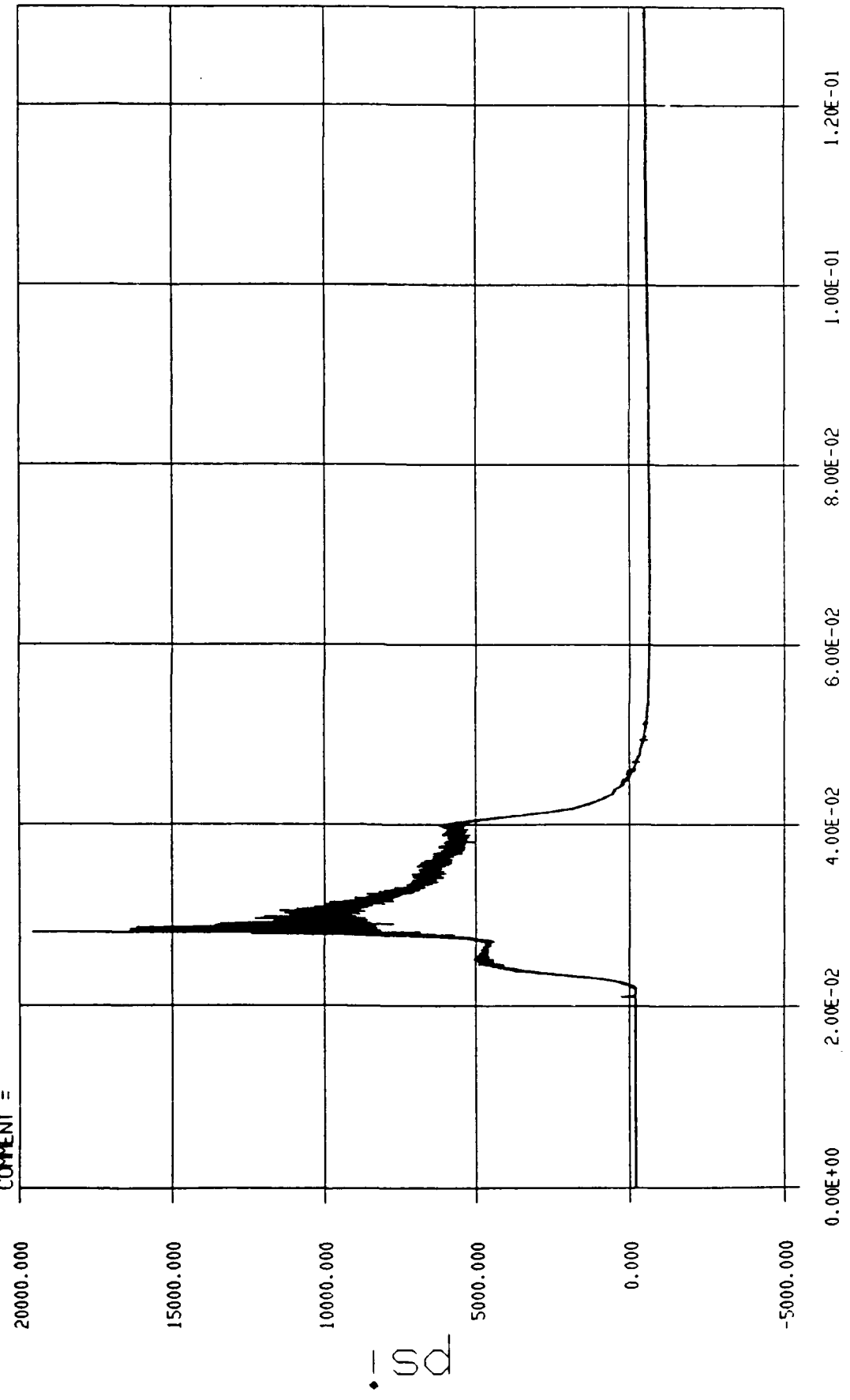
P21.LR1





START SAMPLE = 1  
ENDING SAMPLE = 131072  
# OF SAMPLES = 131072  
SAMPLE INTERVAL = 0.0000E+00  
CAL FACTOR = (psi /VOLT) = 0.0000  
COMMENT =

datap31.001

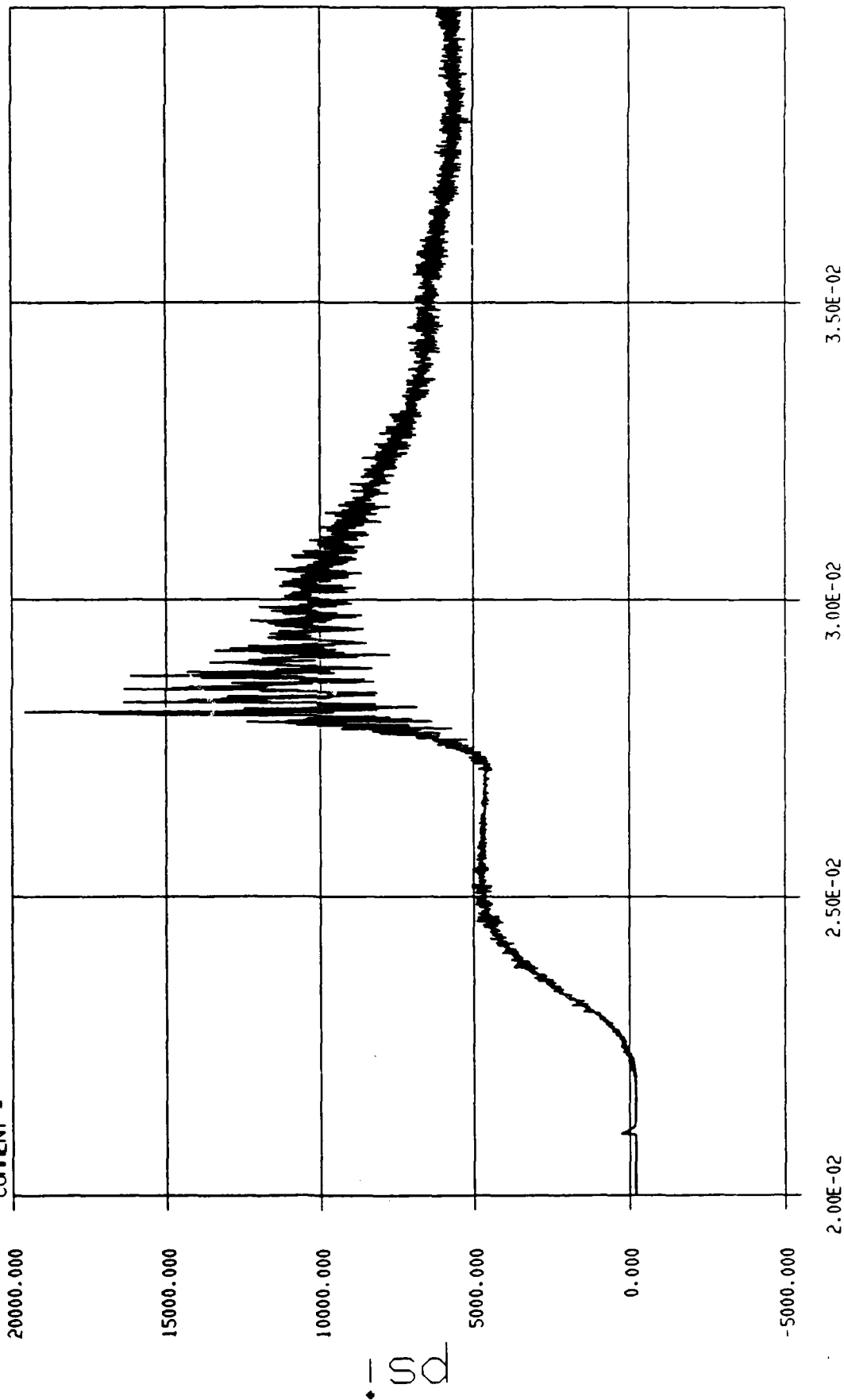




\*\*\*\*\* UNCLASSIFIED \*\*\*\*\*

START SAMPLE = 20000  
ENDING SAMPLE = 40000  
# OF SAMPLES = 20001  
SAMPLE INTERVAL = 0.0000E+00  
CAL FACTOR = (psi /VOLT) = 0.0000  
COMMENT =

datap31.001



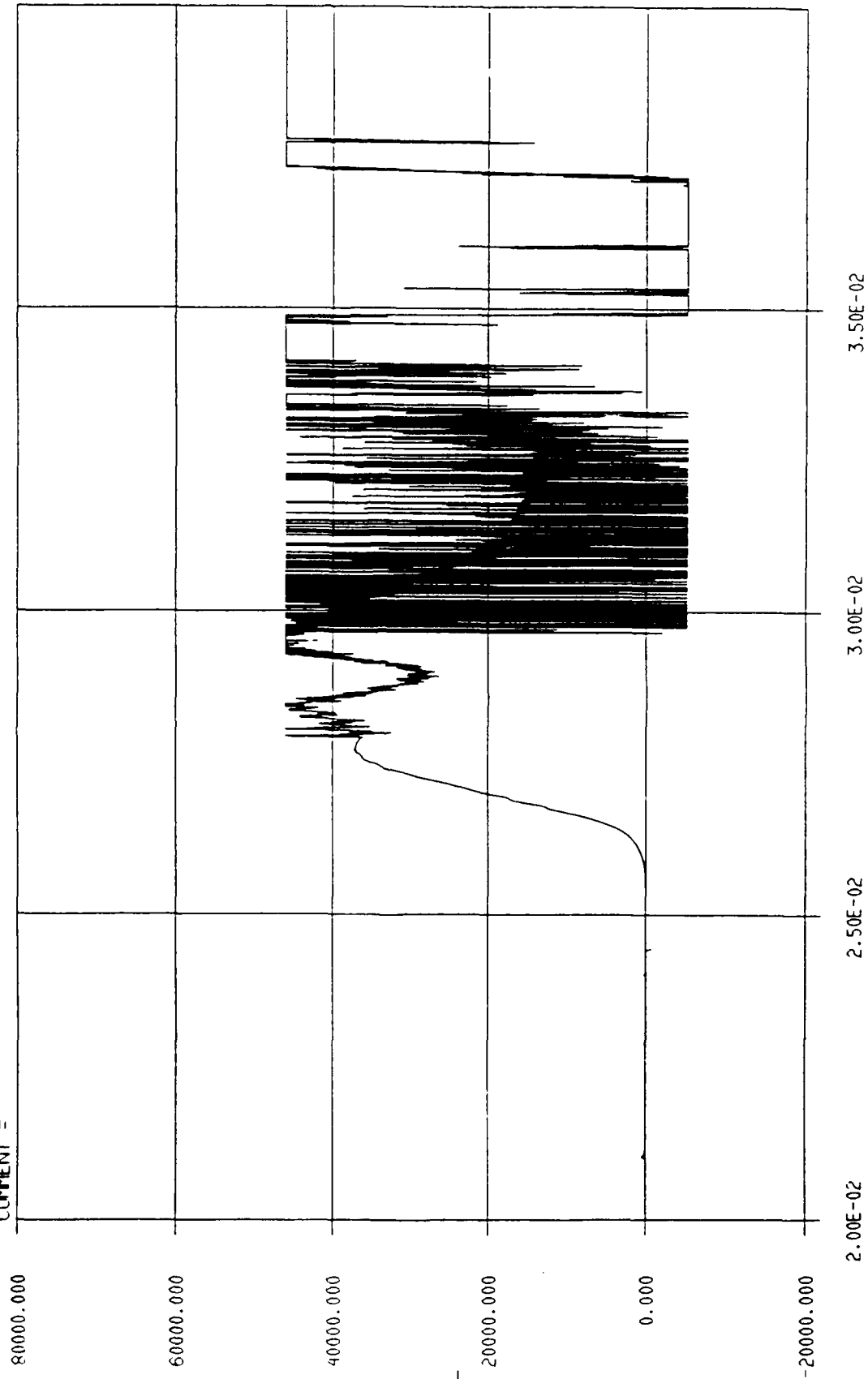
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\*\*\*\*\* UNCLASSIFIED \*\*\*\*\*

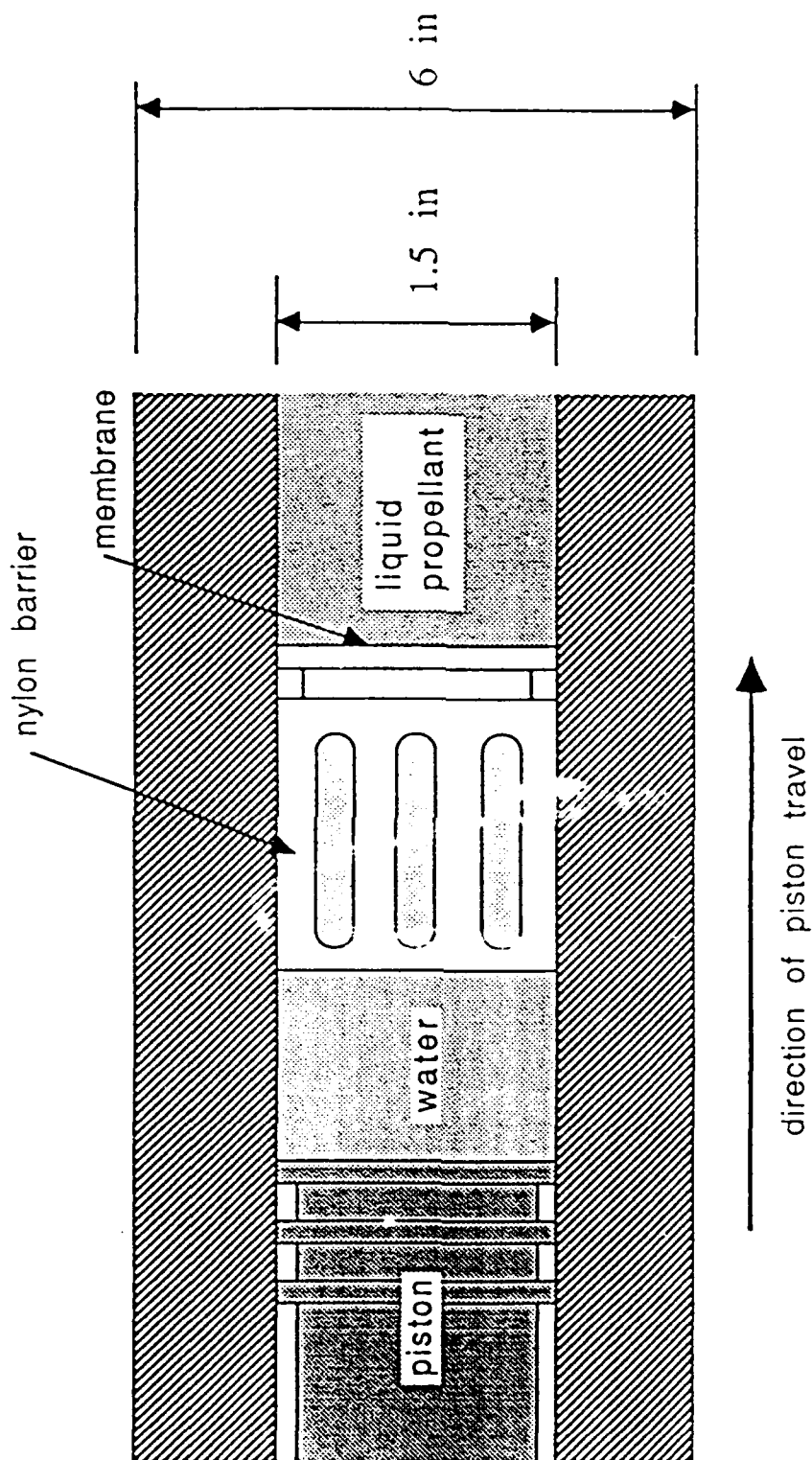
\*\*\*\*\* UNCLASSIFIED \*\*\*\*\*

START SAMPLE = 20000  
ENDING SAMPLE = 40000  
# OF SAMPLES = 20001  
SAMPLE INTERVAL = 0.0000E+00  
CAL FACTOR = (psi /VOLT) = 0.0000  
COMMENT =

datap22.001



## A barrier separates water and liquid propellant



Water flushes the liquid propellant into the combustion chamber and prevents LP from getting between sliding metal surfaces.

## ANALYSES OF THE LIQUID PROPELLANT INJECTOR/COMBUSTOR

Stewart K. Griffiths  
Sandia National Laboratories  
Livermore, California 94551-0969

### ABSTRACT

Sandia National Laboratories has developed and is now testing a liquid propellant injector/combustor (LP I/C) to investigate the injection and combustion of HAN-based propellants at conditions replicating those in a small caliber LP gun. In support of that effort, we have developed a kinematic model of the LP/IC operation, with the intent to provide design guidance and aid in interpreting experimental results. This simplified model simulates basic LP I/C operation, including start-up transients, injection rates, and propellant and combustion chamber pressure histories, and further, allows modeling those pressure oscillations which arise from the coupling between the injection and combustion processes. Acoustic phenomena, leading to pressure oscillations which arise solely within the combustion chamber, are specifically excluded from the model.

The LP I/C model closely follows previous analyses which are based on a lumped-parameter approach. The core of the model is the injector piston motion, which is described by the piston acceleration and a simple force balance, and mass conservation equations for the propellant and driver gas. These basic conservation equations are supplemented with three additional equations describing the triggering process, and the resulting system of ordinary differential equations are integrated forward in time using a backwards differentiation algorithm suitable for stiff problems.

Sample calculations for the LP I/C show the effect of the injection orifice size on the liquid propellant and combustion chamber pressure histories. As the injection orifice is increased from 5 to 9 mm, the steady portion of the combustion chamber pressure increases from 240 MPa to about 340 MPa, and the period of injection falls from 20 ms to 13 ms. Similar calculations demonstrate the effect of combustion chamber volume, burst disk pressure and exit nozzle size on the LP I/C performance. The effect of trigger by-pass tube diameter on post-burst pressure drop following burst disk rupture is also examined. These results were used to establish the baseline LP I/C design.

# KINEMATIC MODELING OF THE LIQUID PROPELLANT INJECTOR / COMBUSTOR

Stewart K. Griffiths  
Sandia National Laboratories  
Livermore, California



## MOTIVATION

---

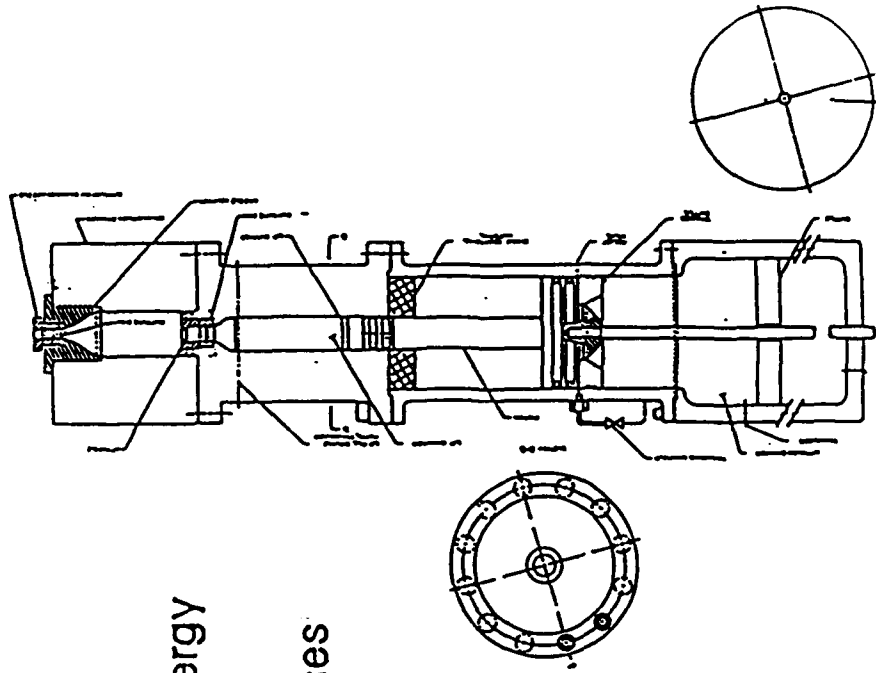
- PROVIDE DESIGN GUIDANCE FOR LP INJECTOR/COMBUSTOR
  - AID IN INTERPRETING EXPERIMENTAL RESULTS
- 

CURRENT MODELING EFFORT IS NOT INTENDED TO ADDRESS CHEMISTRY OF COMBUSTION, JET BREAKUP, ACOUSTIC PHENOMENA, ETC.

# PHYSICAL MODEL OF INJECTOR / COMBUSTOR

---

- CONSERVATION EQUATIONS
  - piston momentum  $f=ma$
  - driver gas mass, momentum and energy
  - propellant mass and momentum
  - mass and energy of combustion gases
- CONSTITUTIVE RELATIONS
  - dampers  $U$  and  $U^2$
  - finite rate of combustion  $aP^n$
  - compressibility of propellant and  
damper fluids
  - constant injection friction factor
  - choked flow in combustor nozzle



## LP INJECTOR / COMBUSTOR APPROXIMATES SMALL-BORE REGENERATIVE GUN ENVIRONMENT

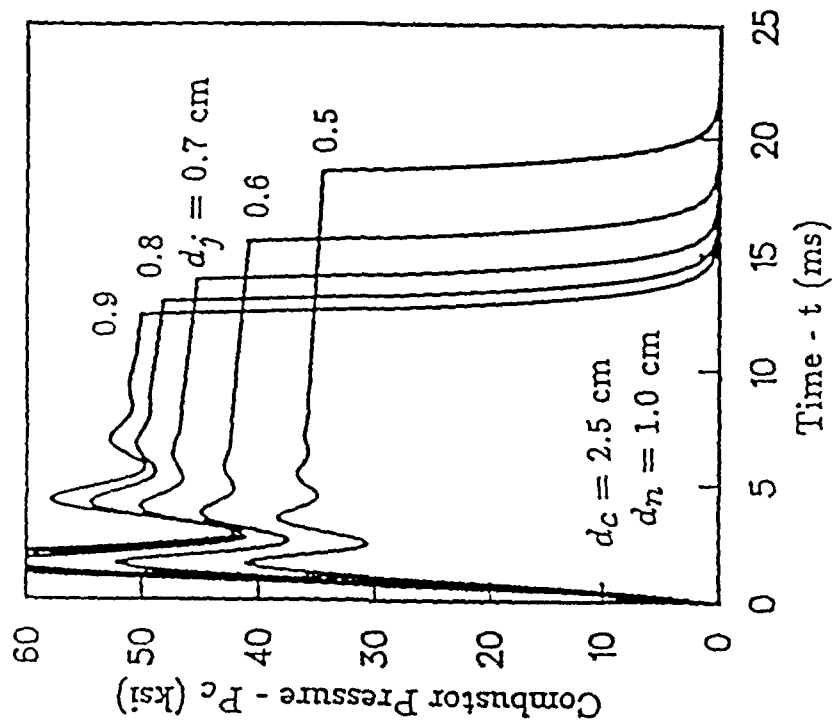
- TARGET OPERATING CONDITIONS

- combustor pressures to 50 ksi
- 0.5 lbm propellant mass
- 10-20 ms period of operation
- steady operation for 5-10 ms

- OPERATING CONDITIONS FIX

### GEOMETRY OF DESIGN

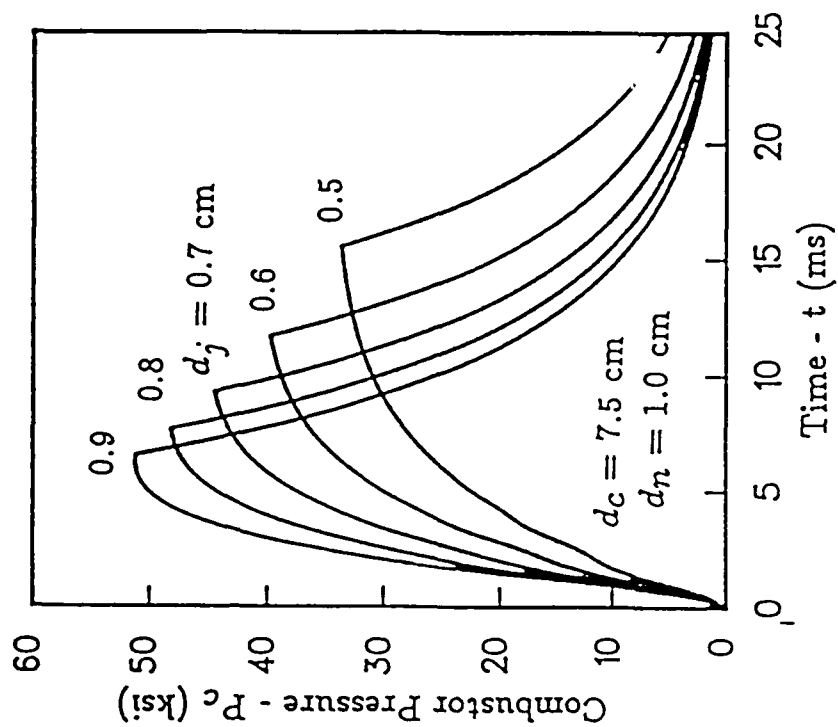
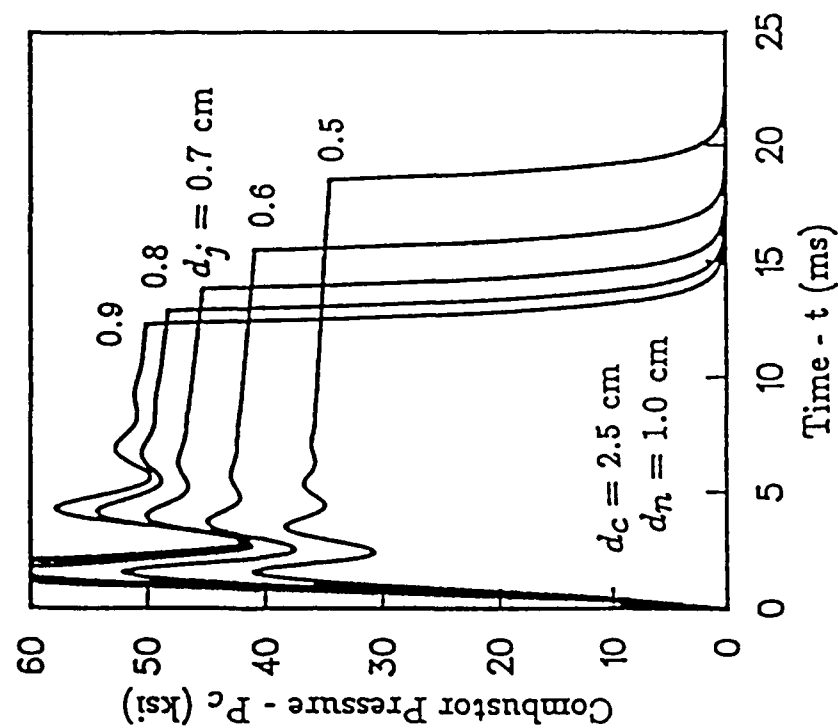
- driver and injector pistons
- injector and combustor nozzles
- combustor volume





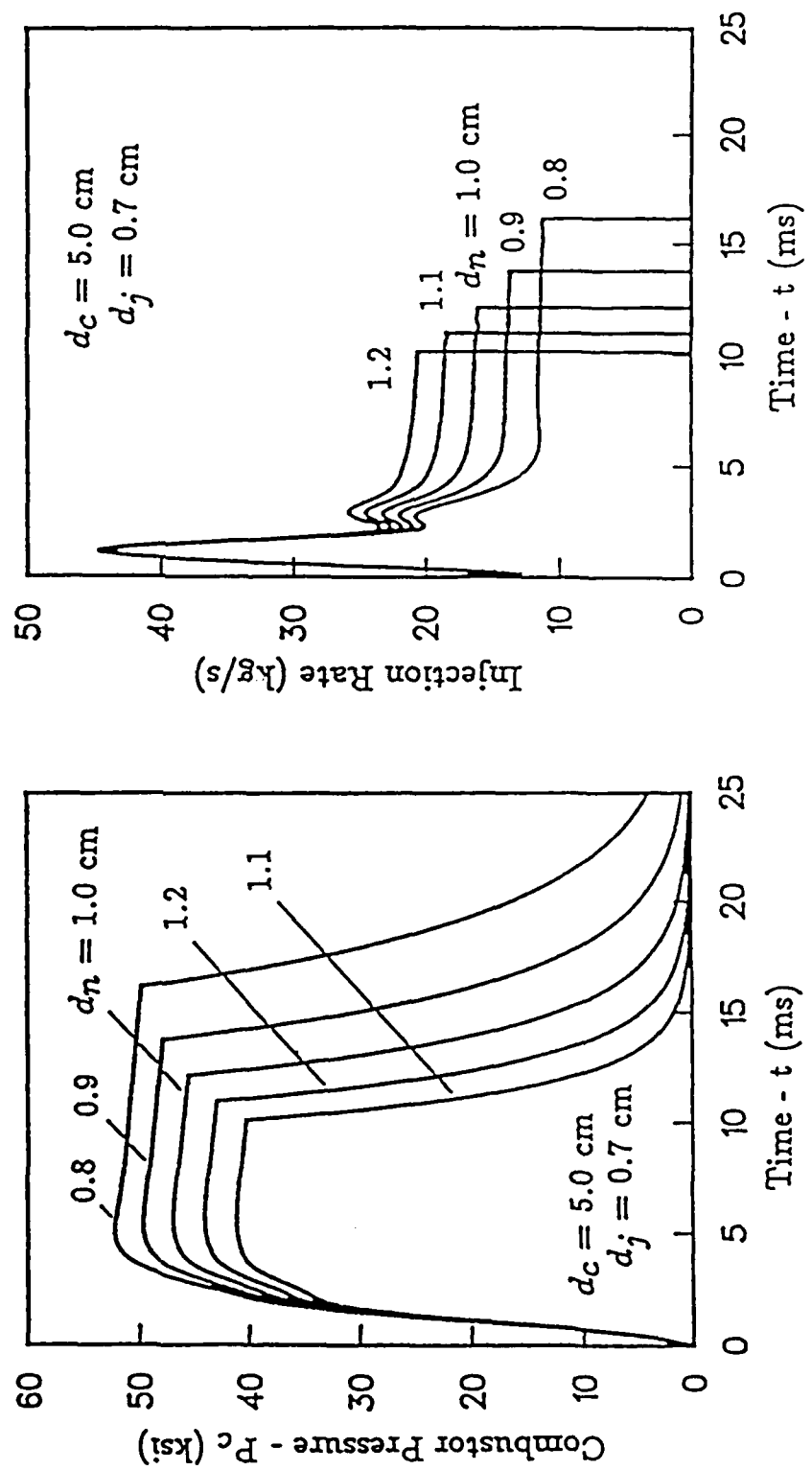
## PARAMETRIC STUDIES HELP EVALUATE DESIGN

- BASELINE DESIGN • piston stroke - 15 cm • driver piston - 130 cm<sup>2</sup>
  - injector piston - 11 cm<sup>2</sup> • combustor length - 10 cm
- EXAMINE EFFECT OF COMBUSTOR DIAMETER • 2.5 cm Vs 7.5 cm



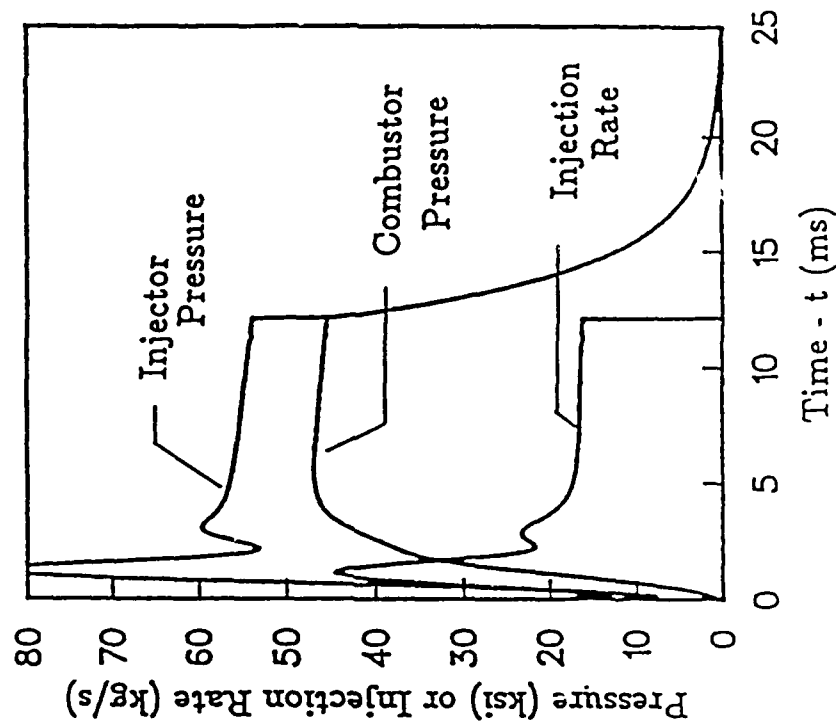
## PARAMETRIC STUDIES (CONT.)

- NOW EXAMINE EFFECT OF COMBUSTOR EXIT NOZZLE THROAT



## RESULTS OF PARAMETRIC STUDY

- INITIAL DESIGN VALUES
  - injector diameter - 0.7 cm
  - combustor nozzle - 1.0 cm throat
  - combustor volume - 210 cm<sup>3</sup>
- CALCULATED OPERATION
  - combustor pressures to 47 ksi
  - 12 ms period of operation
  - peak piston speed - 36 m/s  
steady speed - 7 m/s
  - peak injection rate - 44 kg/s  
steady rate - 16 kg/s
  - steady operation for 8 ms
  - peak injection pressure - 84 ksi



## ANALYSES OF START-UP TRANSIENTS

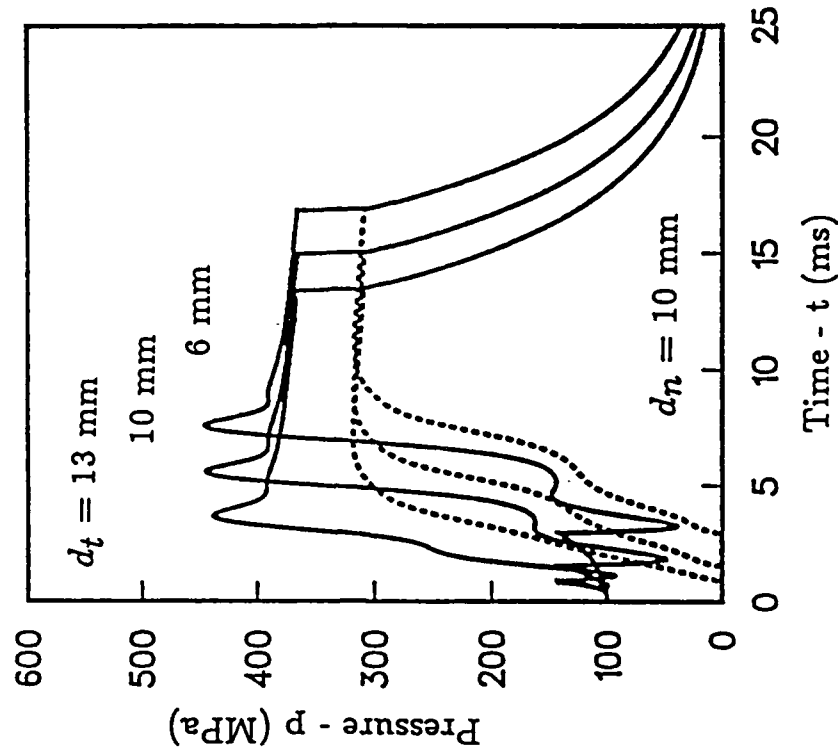
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- **EARLY TRANSIENTS MAY LEAD TO FLASH-BACK**

- burst disk rupture at low piston speed
- sudden drop in LP pressure
- reduced injection velocity
- flash-back into LP chamber

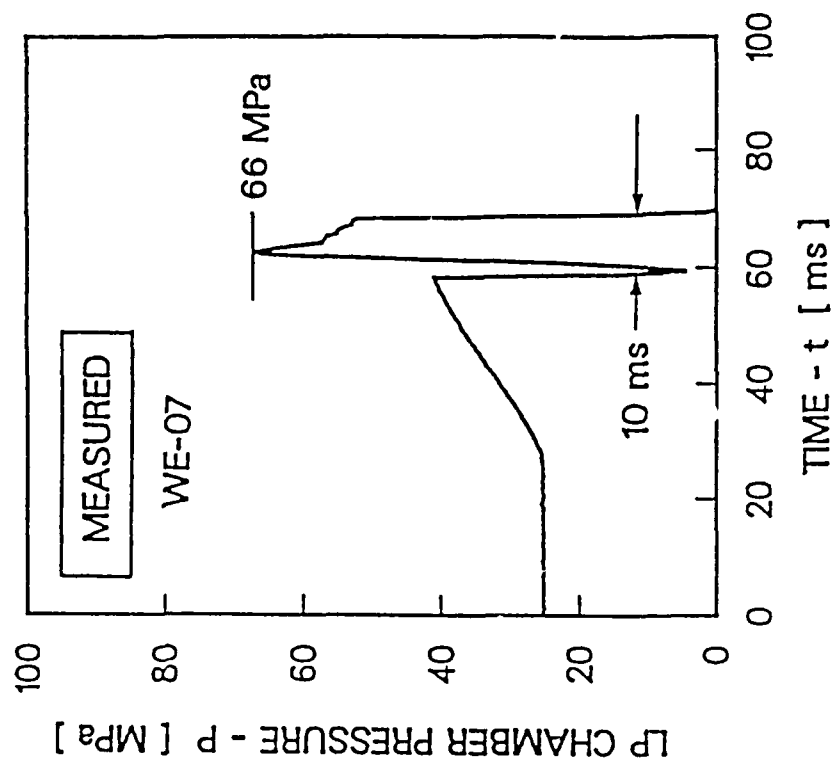
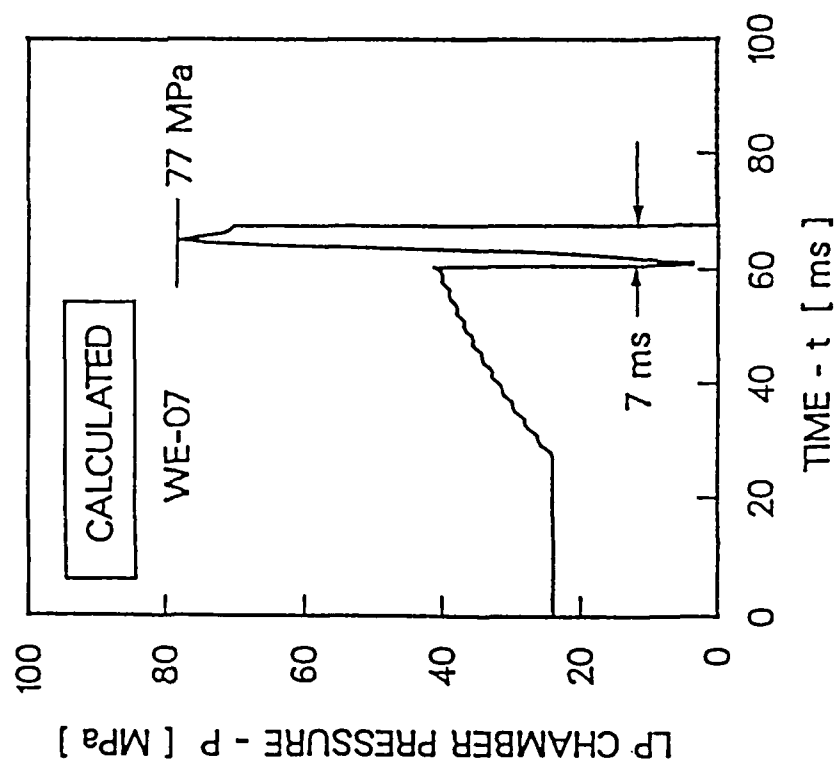
- **IMPROVED DESIGN CAN REDUCE POST-BURST PRESSURE DROP**

- mechanical trigger
- increased heel taper
- face seal on trigger volume
- pre-trigger piston motion
- larger trigger tube



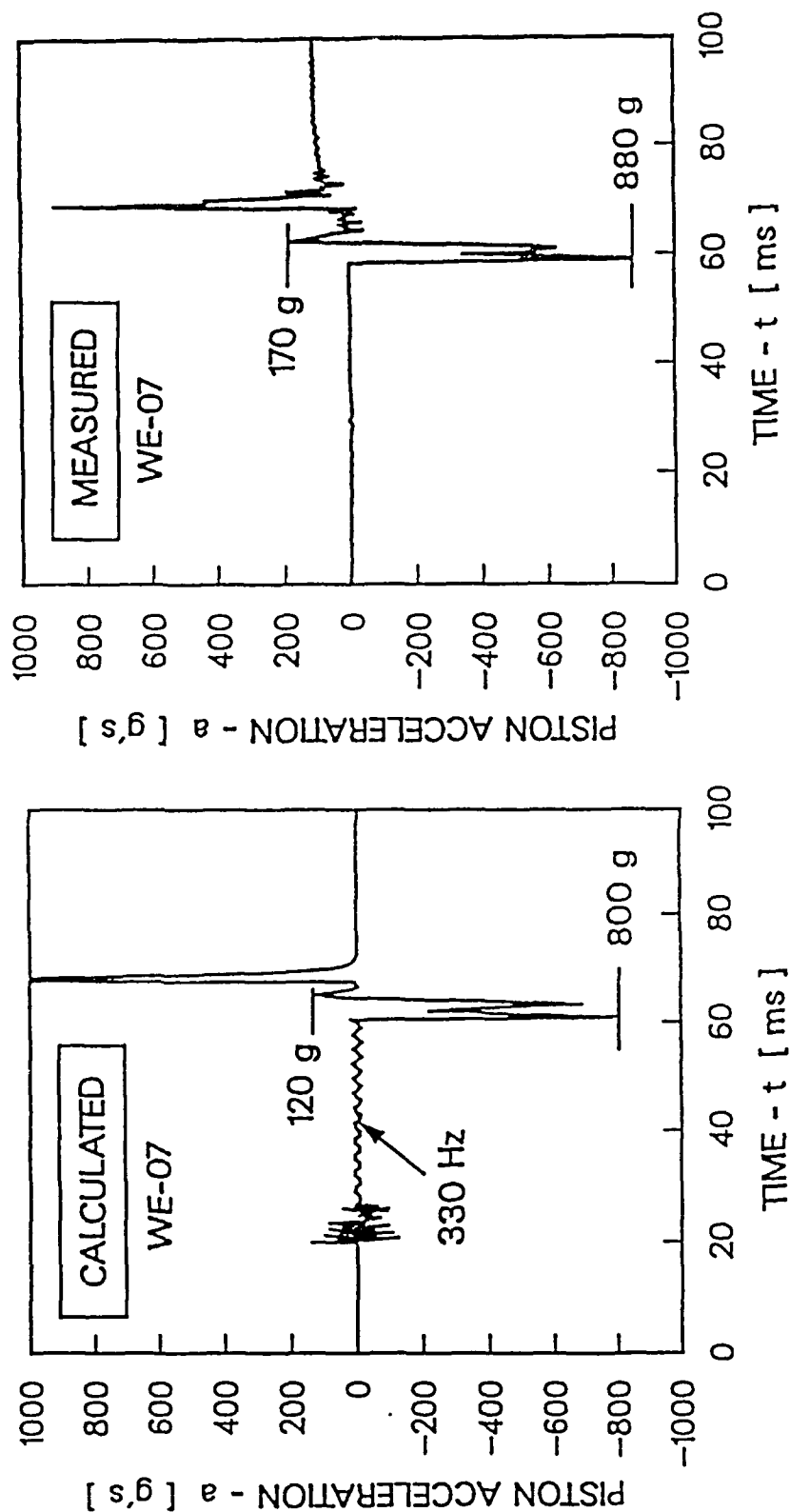
# COMPARISON BETWEEN CALCULATED AND MEASURED LP CHAMBER PRESSURES

- WATER INJECTION TEST - DRIVER PRESSURE OF 7 MPa
- INJECTION TO AMBIENT PRESSURE THROUGH 5 MM ORIFICE



# COMPARISON BETWEEN CALCULATED AND MEASURED PISTON ACCELERATIONS

- WATER INJECTION TEST - DRIVER PRESSURE OF 7 MPa
- INJECTION TO AMBIENT PRESSURE THROUGH 5 MM ORIFICE



## SUMMARY / FUTURE EFFORTS

---

- COMPLETE DETAILED ANALYSIS OF TRIGGER MECHANISM
  - redesign stepped piston for smooth release
  - eliminate start-up transients in injector pressure
- EXAMINE EFFECTS OF FINITE COMBUSTION RATE
- CONTINUE CALCULATIONS FOR DESIGN OF INSTRUMENTATION
- BEGIN MORE DETAILED ANALYSES OF INJECTION AND COMBUSTION PROCESSES

## REACTIONS OF THE HYDROLYZED LIQUID PROPELLANT

HEATHAN, R. L. 1971

The liquid propellants consisting of hydrazine, ammonium nitrate (HAN), triethanolammonium nitrate (TEAN), and water exist as highly structured clusters surrounded by regions of essentially unorganized water. HAN exists in these clusters as an ion-pair and the cluster is organized by virtue of extensive hydrogen bonding. Many of the observed physical properties of the propellants reflect this structure and the equilibrium between the clusters and the unorganized water that surrounds them.

Reaction of the propellants is sequential with HAN reacting first. Thermal decomposition of HAN is initiated by hydride ion transfer from hydroxylammonium to nitrate and produces the nitroxyl radical and nitrous acid. These intermediates then react with HAN and produce nitrous oxide, nitrogen, nitric acid. Heat is liberated and, in the later stages of reaction, a gas cloud consisting of the HAN reaction products surrounds TEAN droplets. Combustion involves the vigorous reaction of these droplets with the oxidizing species in the gas cloud. Approximately 80 % of the energy of the propellant is released during the combustion sequence.

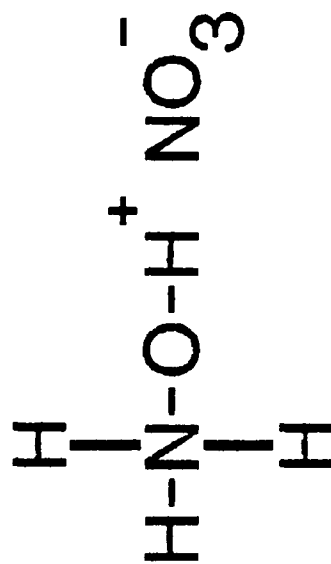


# THE HAN-BASED PROPELLANTS HOW AND WHY THEY REACT

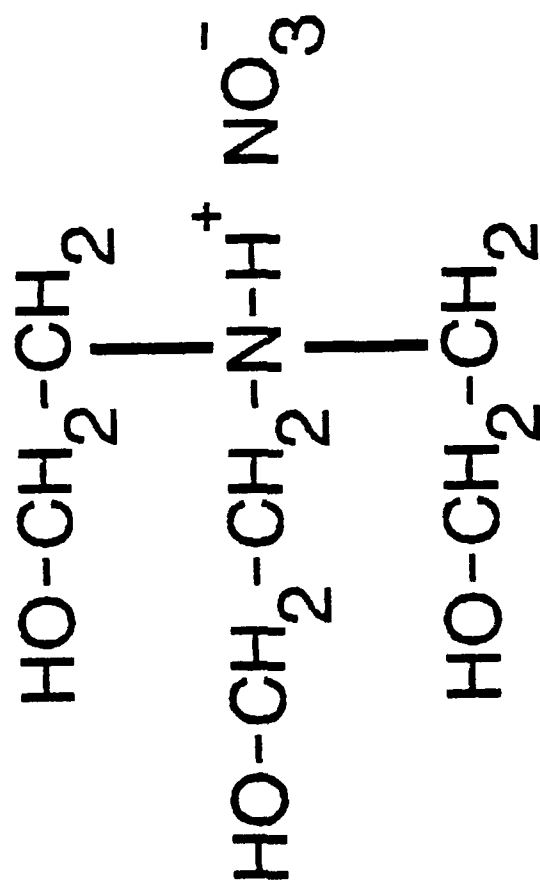
**NATHAN KLEIN**

**USA Ballistic Research Laboratory  
Aberdeen Proving Ground  
Maryland**

# HYDROXYLAMMONIUM NITRATE (HAN)

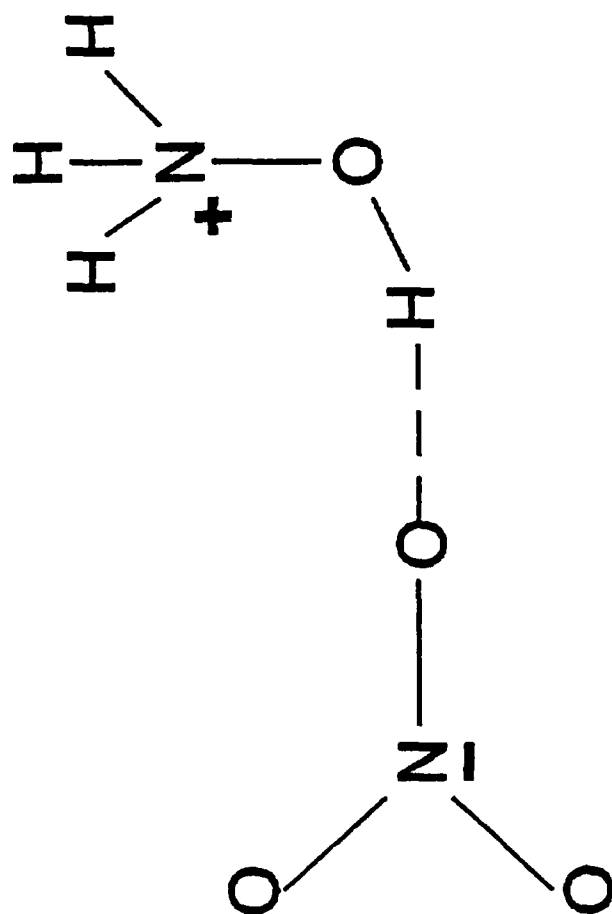


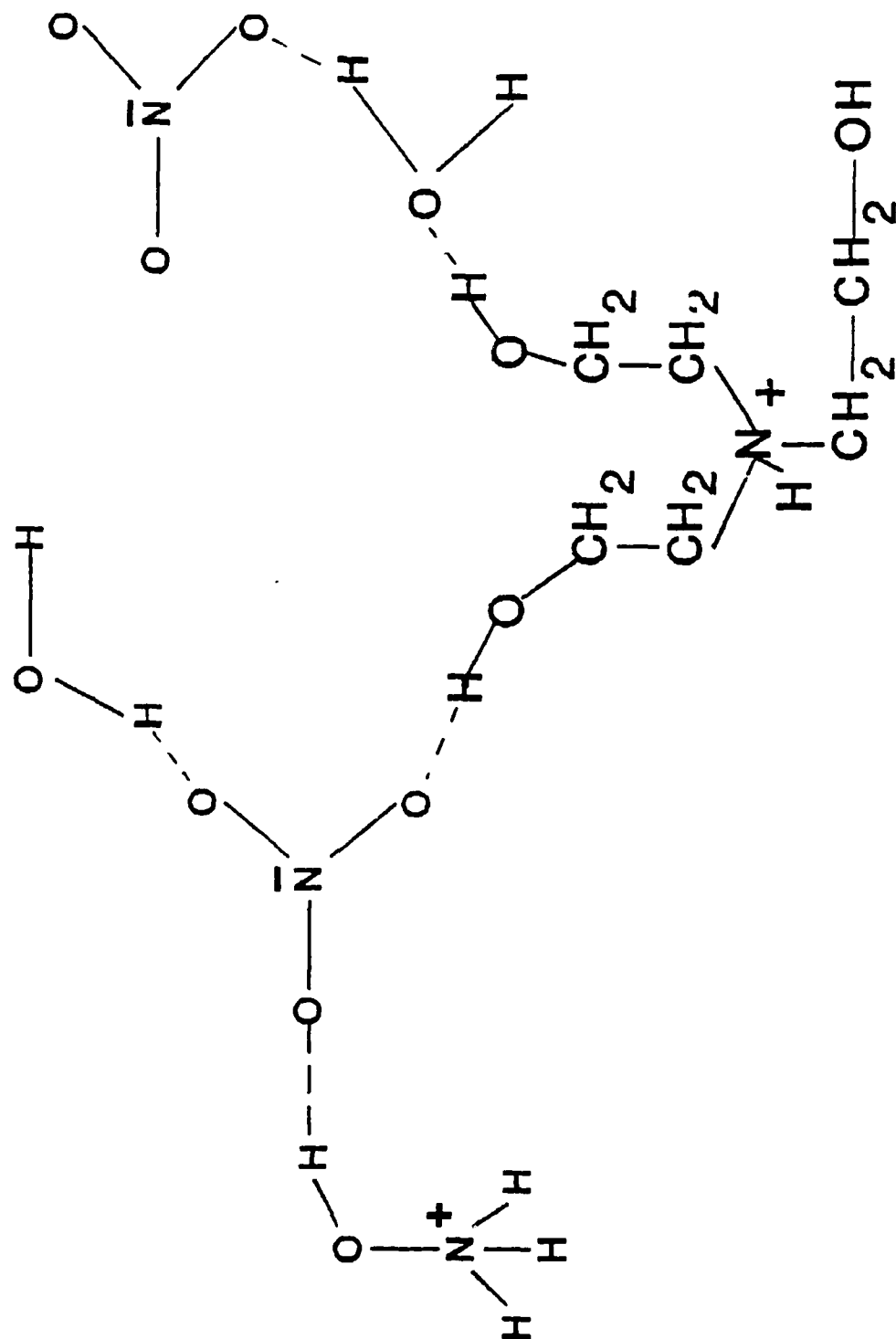
# TRIETHANOLAMMONIUM NITRATE (TEAN)

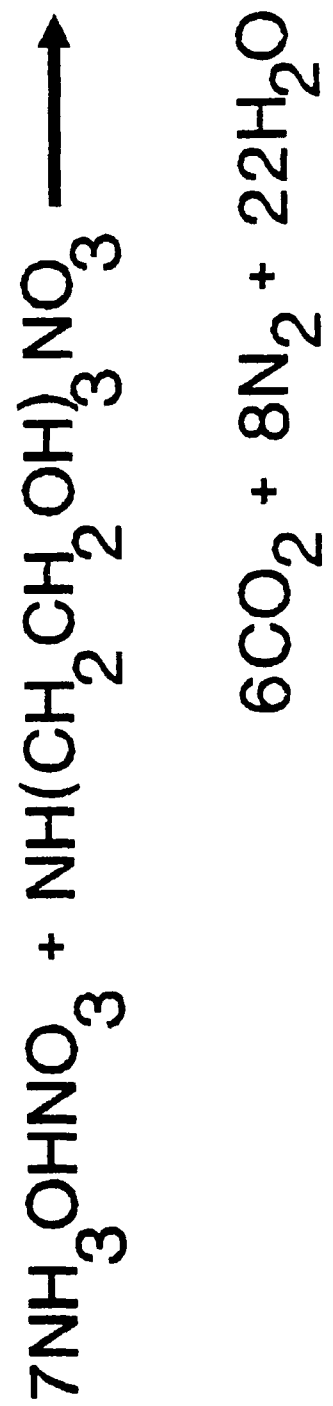


# PROPELLANT COMPOSITION

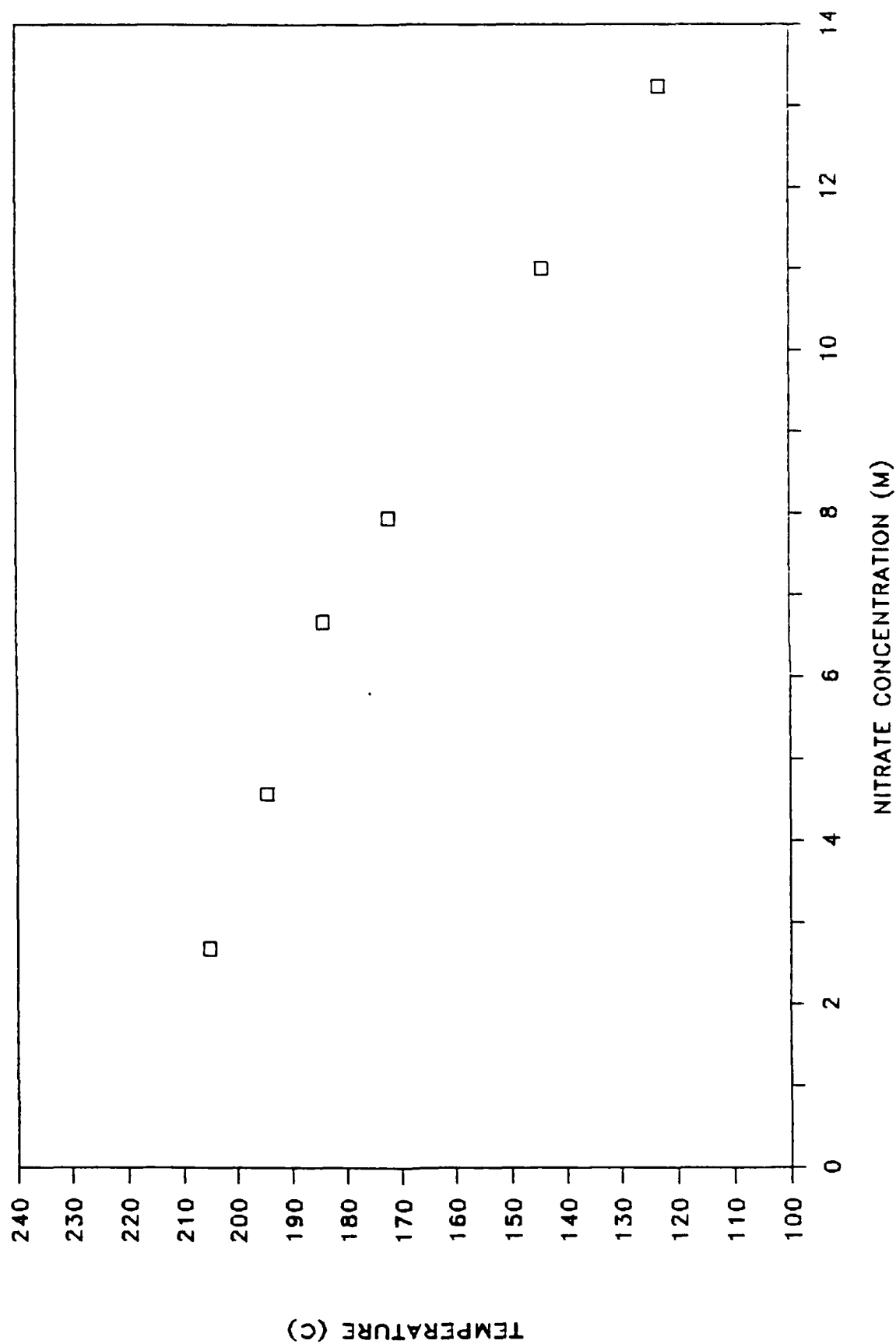
	HAN	TEAN	Water
LGP1845	9.63 M	1.38 M	ca 13.6 M
LGP1846	60.8 %	19.2 %	20.0 %







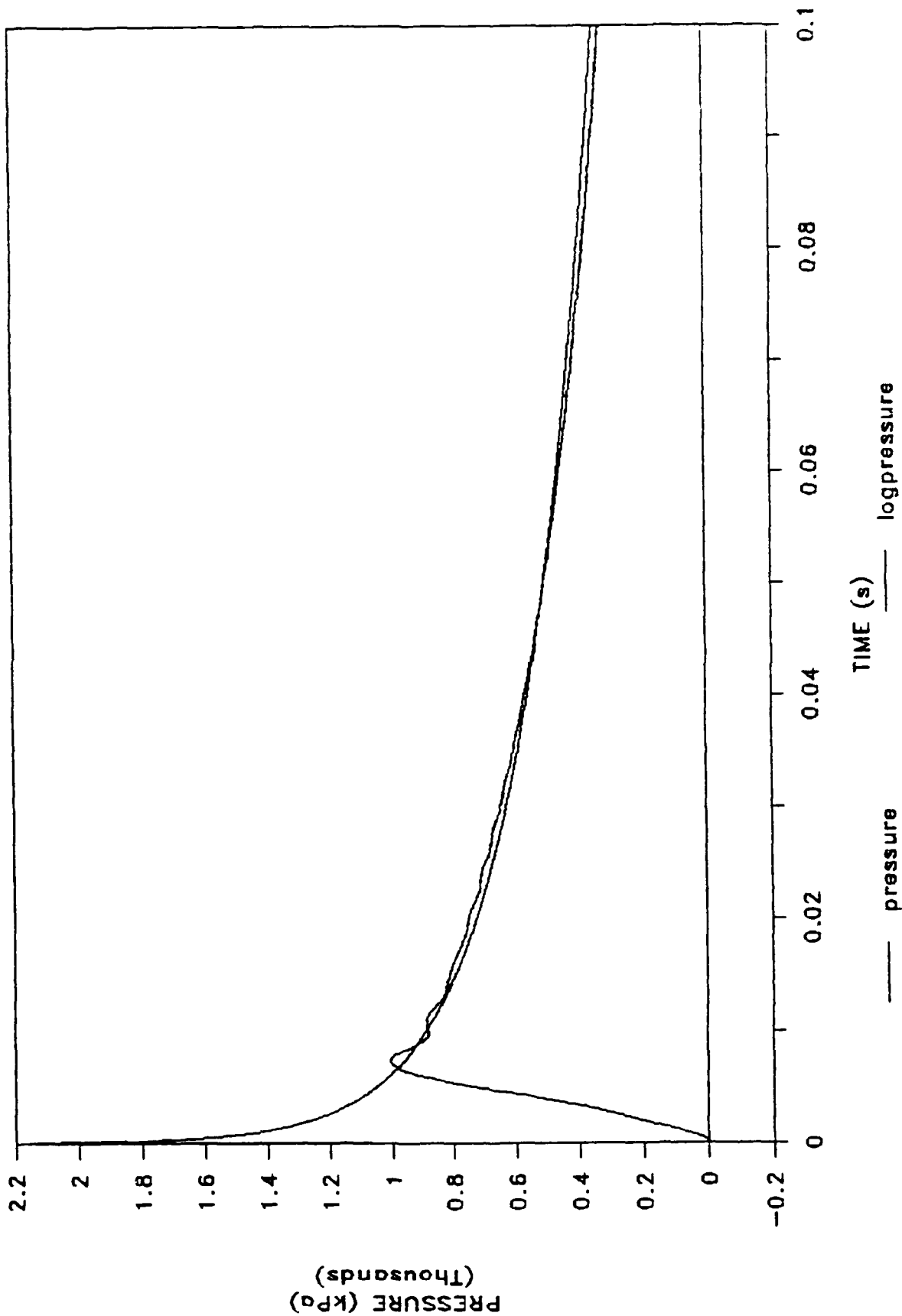
# INITIATION TEMPERATURE





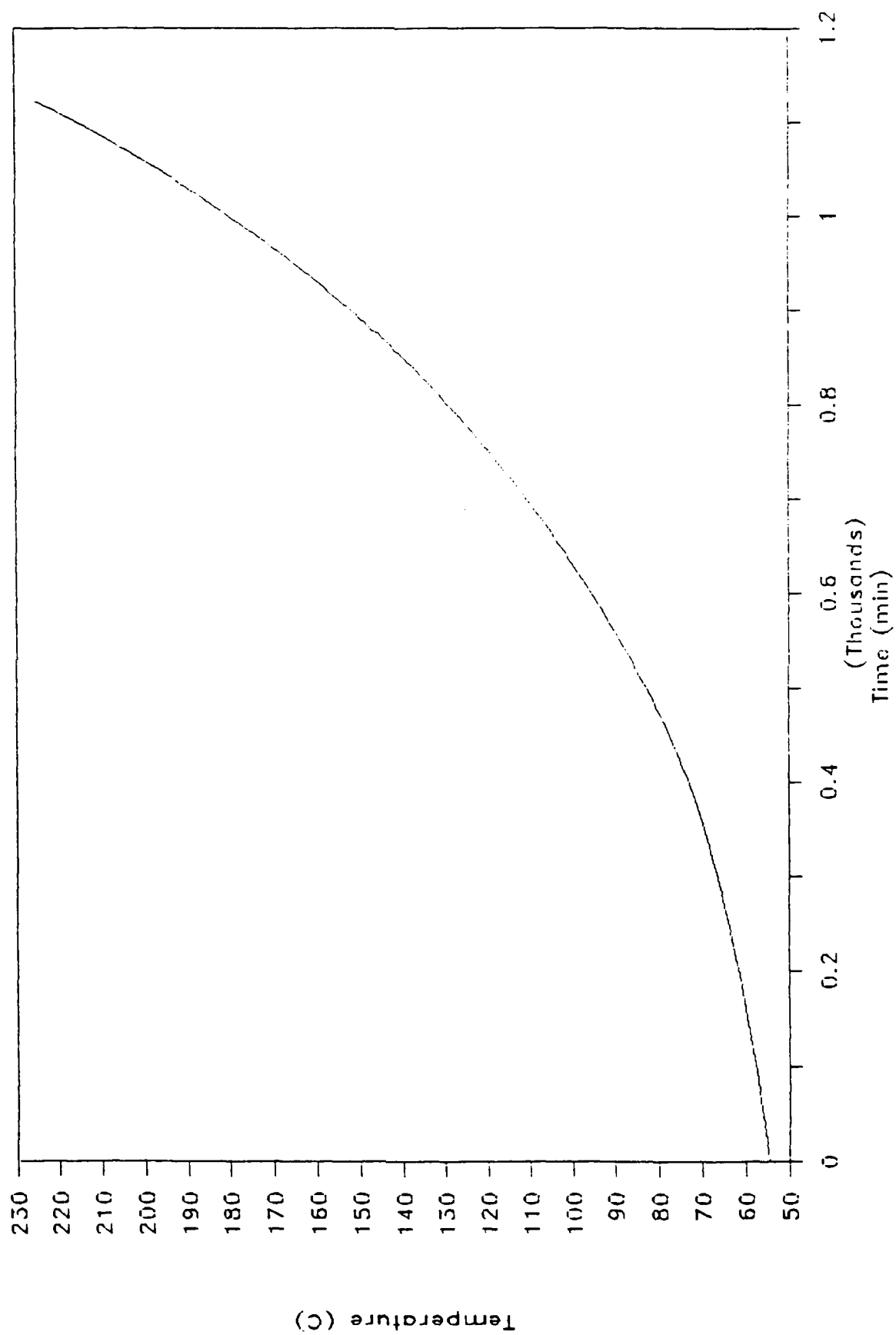
# LPG1846

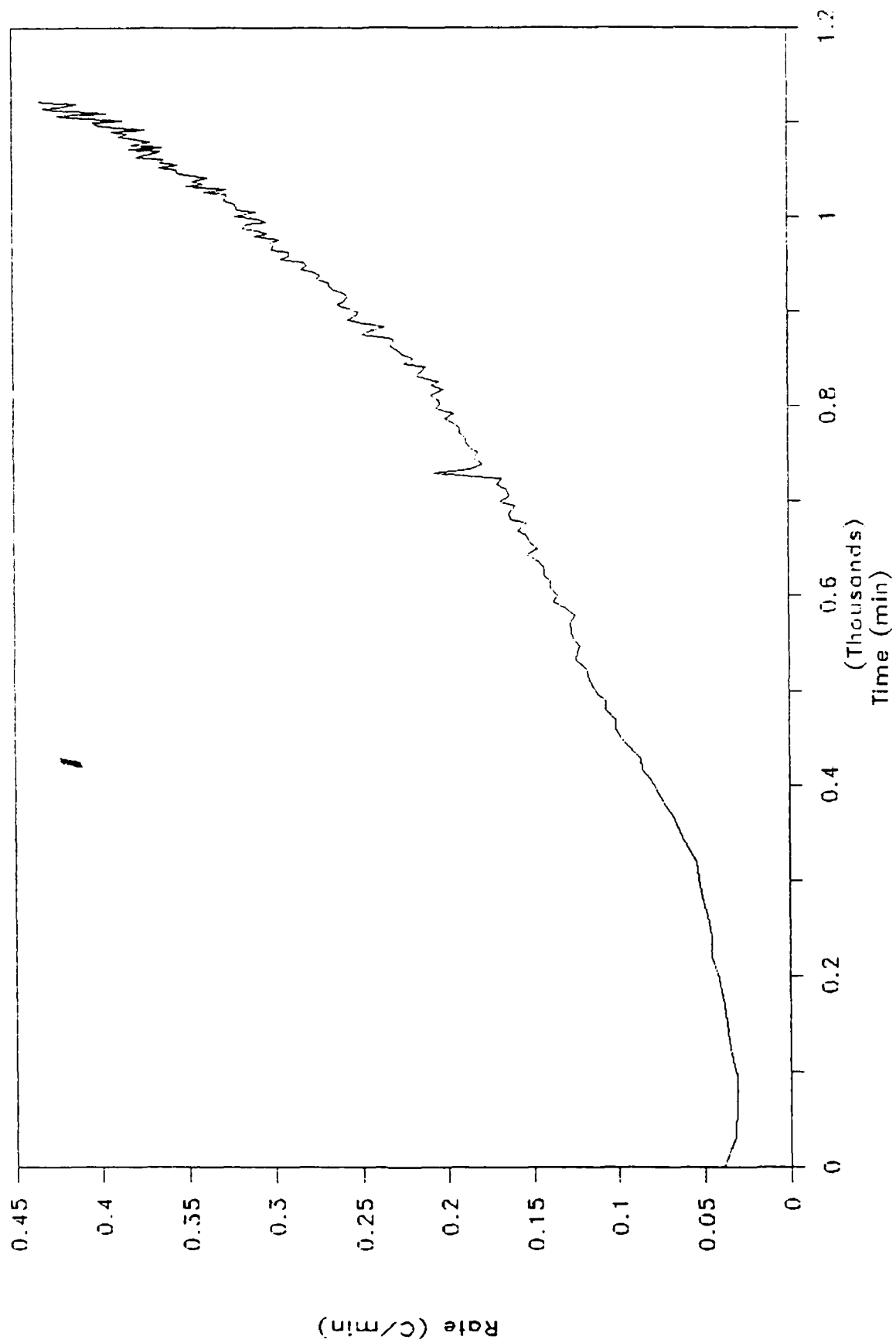
## PRESSURE AND LOGPRESSURE



# ARC Reaction Sequence

Exotherm (C)	Event
122	HAN decomposition
180	Nitric acid decomposition
220	TEAN decomposition



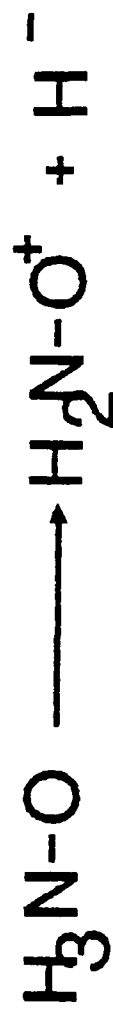
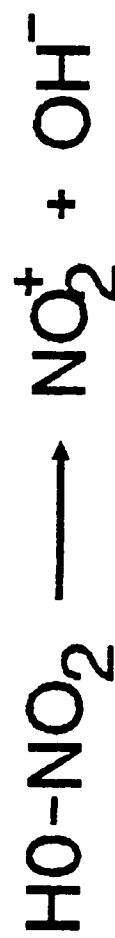
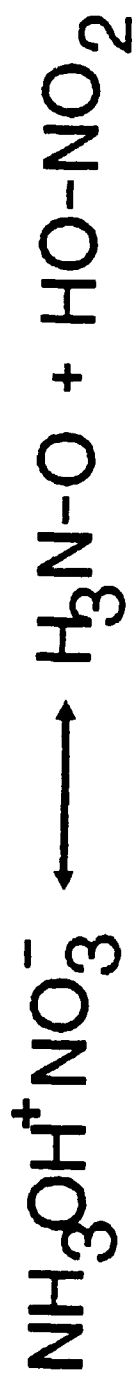


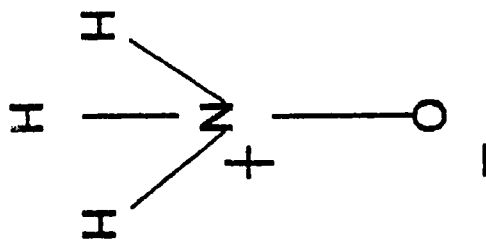
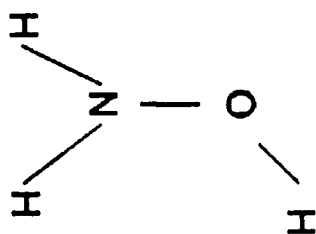
# PROPELLANT IGNITION (1)

## HAN REACTS FIRST

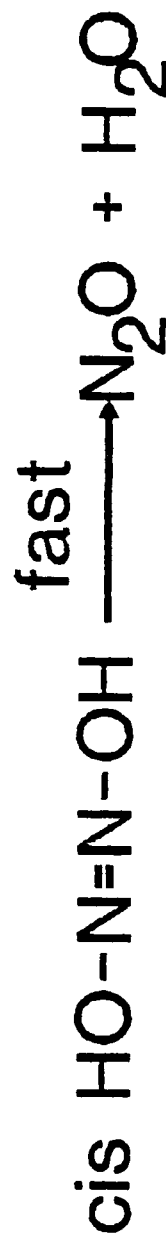
- Liquid Phase Reaction
- Products
  - Nitrogen
  - Nitrogen oxides
  - Nitric acid
  - Water
  - HEAT

## REACTIONS (1)



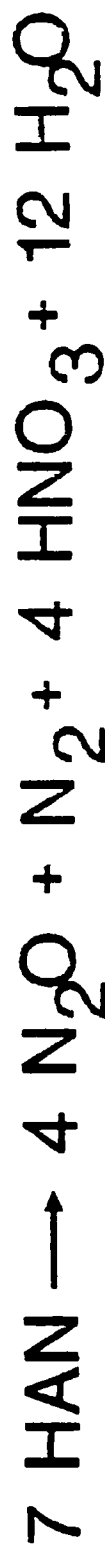
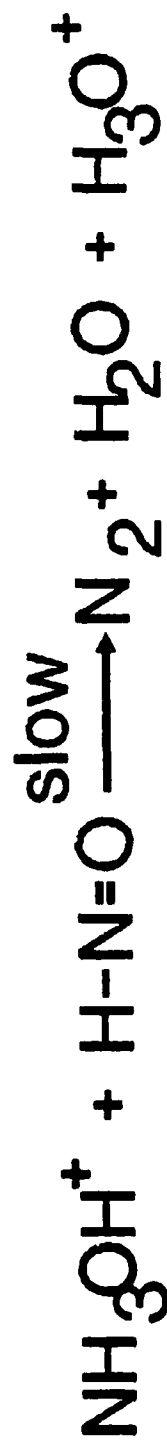


## HO-NO REACTIONS





## HN=O REACTIONS



# PROPELLANT IGNITION (2)

## TEAN REACTS LATER

- Two Phase Reaction  
TEAN droplets  
Nitrogen oxides (gas)  
Nitric acid (gas)
- Products  
Nitrogen  
Carbon dioxide  
Water

# CONCLUSIONS

- Reactions are sequential
- HAN reacts first
- HAN reaction is homogeneous, liquid phase
- TEAN reacts later
- TEAN reaction is two-phase  
TEAN droplets react with oxides of nitrogen  
and with nitric acid (gas)

SUGGESTED SPECIFICATIONS FOR  
HAN-BASED LIQUID PROPELLANTS

R. A. BIDDLE  
THIOKOL CORPORATION  
ELKTON DIVISION  
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301-392-1237

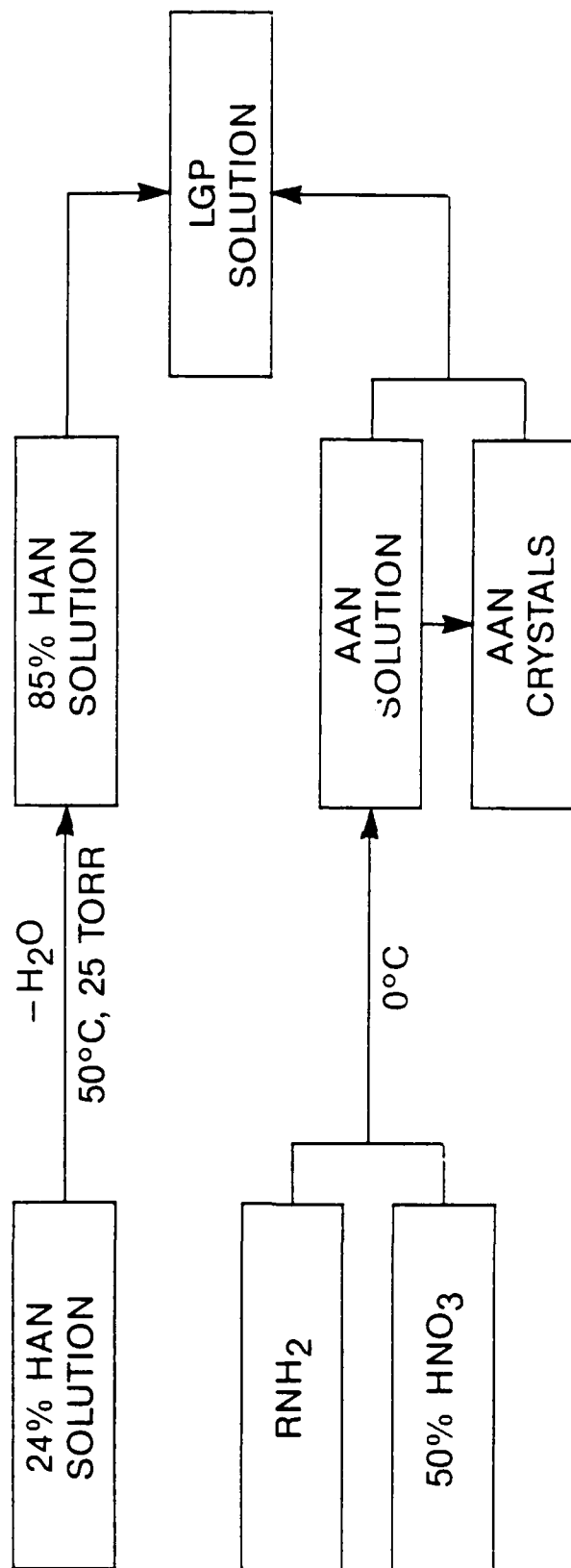
The current specifications for liquid gun propellants (LGP) based upon hydroxylammonium nitrate (HAN) are fairly loosely defined. At the present time these have been developed as the propellants have been prepared in laboratory thru pilot plant scale batches and as stability and use studies have been accomplished. The propellant LGP1846 has been selected as the example for developing revised specifications since approximately 15,000kg of this material have now been prepared for delivery. This material has been used for numerous studies and for most, if not all, of the actual gun firing tests to date.

Specifications for LGP1846 include content, analyses used and packaging of the final material. Originally the content of each of the components (HAN, triethanolammonium nitrate or TEAN and  $H_2O$ ) were specified to be within  $\pm 0.5\%$  by weight of the required concentration. It is suggested that this be expanded to include the total nitrate content and the ratio of the HAN to the TEAN in the solution. This should provide a better approach toward obtaining the desired 7.0 molar ratio of HAN/TEAN for combustion purposes. The metal ion contamination level has been addressed previously as being desirable to maintain a total of less than 5 ppm of heavy metals. It is anticipated that this can be maintained at the total 5 ppm level with emphasis on the transition metals. An additional specification for a trace of excess acid should be included to promote stability.

The original analyses specified were ultraviolet (UV) spectrophotometry, acid titration and trace metal determination. These have been expanded to include a total water analysis (Karl Fischer) and an oxime/acid titration which allows measurement of both the HAN and the TEAN in the same solution. Trace metal analyses are still required and can be accomplished adequately with atomic absorption (AA) spectrophotometry. The UV analysis provides a single straight forward method for measurement of the total nitrate content. A requirement for examination of the UV trace to define a yellow color component has been lost. The analyses suggested, thus reduce to a standard UV absorption measurement, an oxime/acid titration with aqueous base, a Karl Fischer titration and AA analysis of diluted solutions. Additional work is required to correlate the excess acid level but analysis is straight forward by aqueous base titration.

Packaging of the LGP for shipment has been defined to meet DOT requirements. This includes the actual container for the liquid and the required overpackaging to meet the DOT requirements. While the overpackaging may be altered in the future based upon on going hazard classification tests, the actual container for the liquid will most likely remain the same. Leaching of the polyethylene container is the most important factor. This is required to remove all potential soluble contaminants. The other requirements of a tamper proof and vented closure should still be maintained.

## GENERAL PROCESS SCHEME



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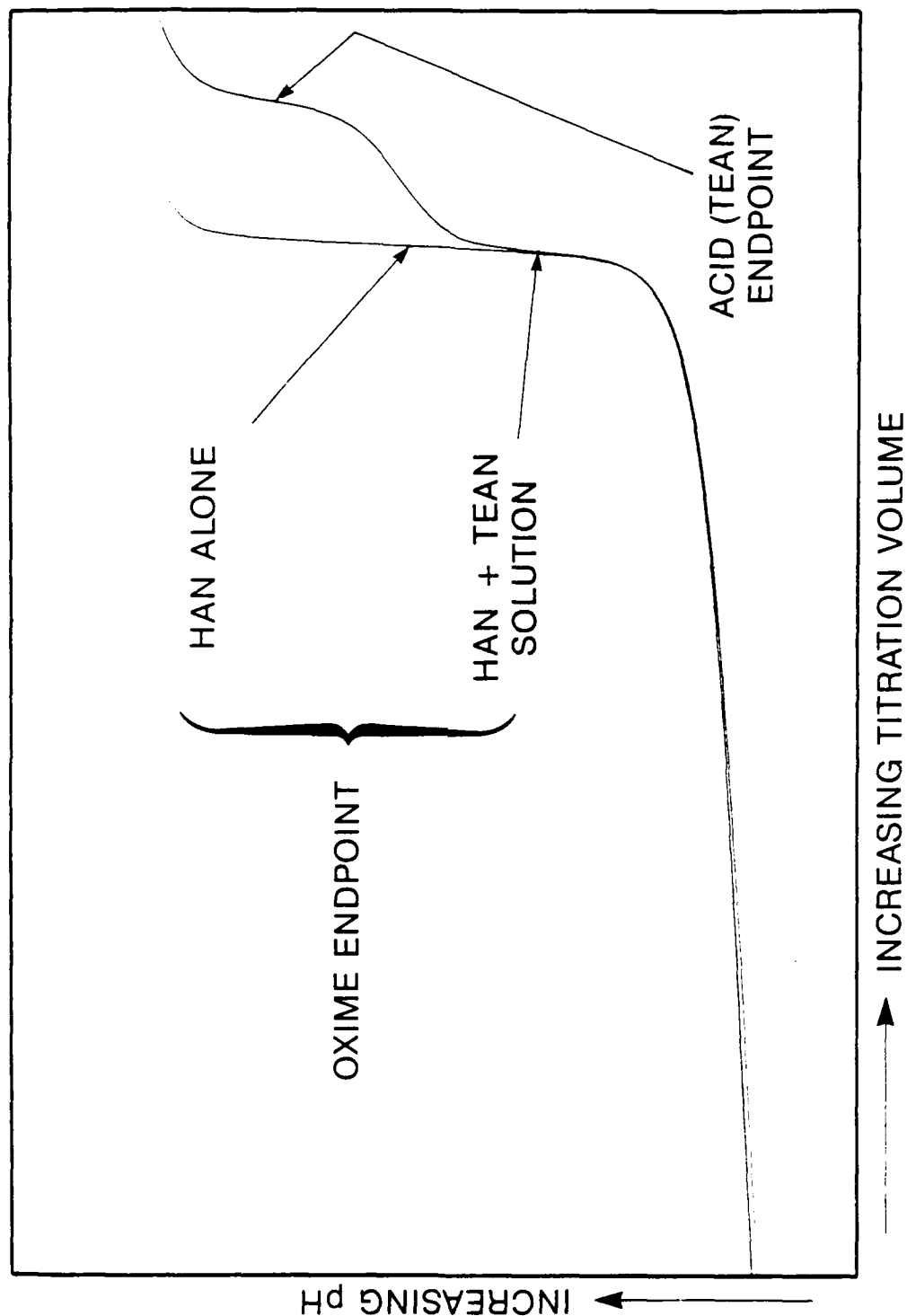
Density	.....	hydrometer
NO <sub>3</sub> <sup>-</sup> content	.....	UV (302 nm)
Water content	.....	Karl Fischer
Amine content	.....	Acid titration
		Oxime titration
Metal contamination	.....	Atomic absorption

**Thiokol** CORPORATION, TACTICAL OPERATIONS, Elkton Division

## H<sub>2</sub>O ANALYSIS — KARL FISCHER

Typical:	Beckman KF4B aquameter
Setting:	40 $\mu$ amps, 30 secs dwell
Burette:	20 ml
Reagent:	Standard or Hydranal (2 mg H <sub>2</sub> O/ml)
Carrier:	1:1 pyridine: CHCl <sub>3</sub>
Sample:	0.2 gram

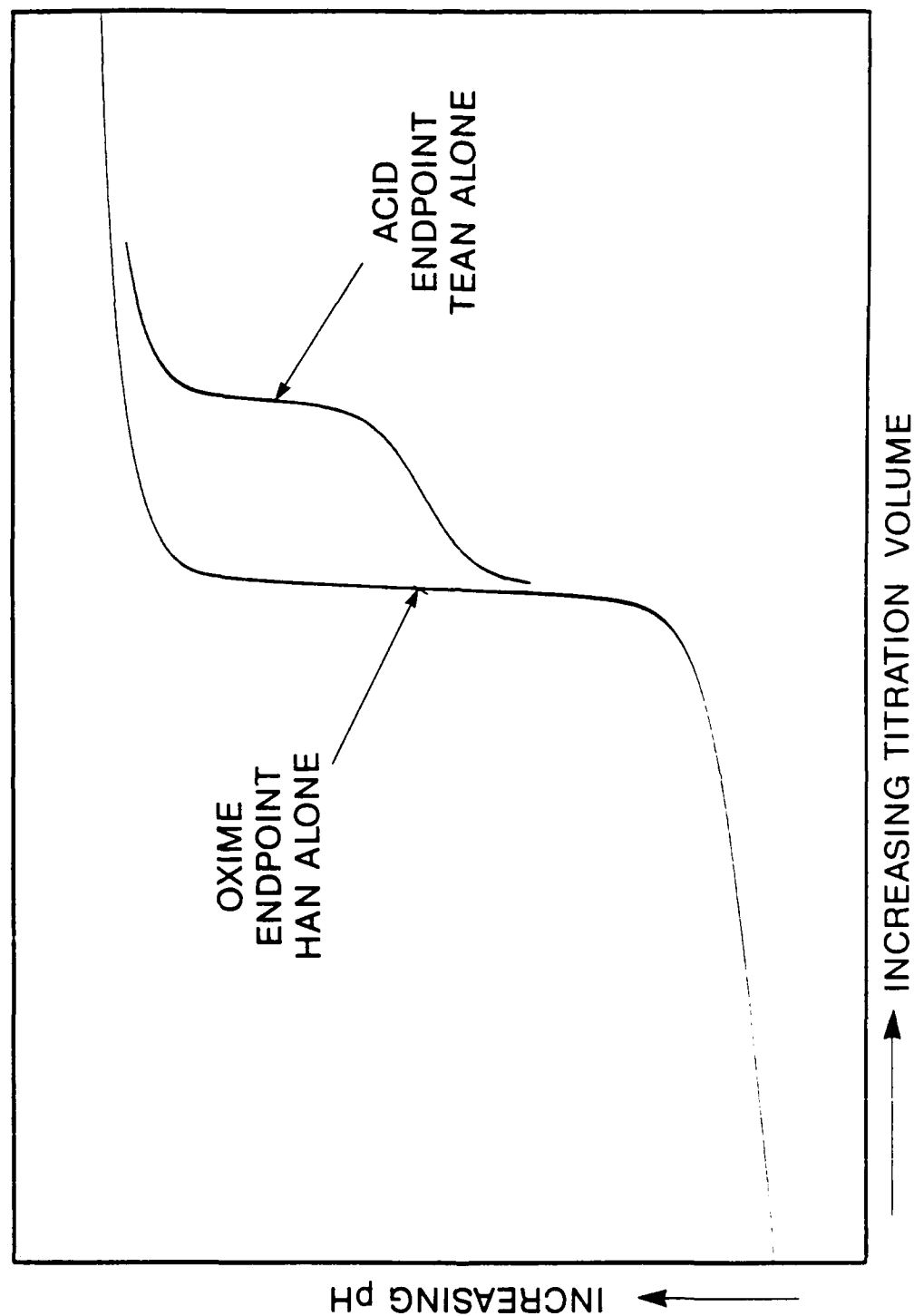
# COMBINED ACID/OXIME TITRATION CURVES



*Thiokol* CORPORATION, TACTICAL OPERATIONS, Elkton Division



## SEPARATE ACID/OXIME TITRATION CURVES



*Thiokol* CORPORATION, TACTICAL OPERATIONS, Elkton Division

## CURRENT LGP 1846 SPECIFICATIONS

### Content:

HAN 60.8  $\pm$  0.5%

TEAN 19.2  $\pm$  0.5%

H<sub>2</sub>O 20.0  $\pm$  0.5%

Metals <5 ppm any heavy metals including Fe, Ni,  
Cu, Pb, Sn

### Analyses:

UV trace (285 to 315 nm)

Karl Fischer titration (H<sub>2</sub>O)

Aqueous NaOH titration in water-acetone

or

Alcoholic butyl amine titration

### Packaging:

Polyethylene, new (virgin), certified for food service

Tamperproof closure

Gas tight to 14.7 psig

# **ANALYSES OF LGP 1846 LOTS**

Lot	Density, g/cc	H <sub>2</sub> O, %	HAN, %	TEAN, %
-01	1.429	19.8	60.3	19.9
-02	1.430	20.3	61.1	19.1
-03	1.432	19.7	61.0	19.6
-04	1.430	20.2	61.1	19.4
-05	1.442	20.5	60.9	19.2
-06	1.434	19.6	61.0	19.5
-07	1.424	20.0	60.7	19.7
-08	1.423	19.6	60.8	19.6
<b>Target</b>				
<b>Max</b>	—	20.5	61.3	19.7
<b>Min</b>	—	19.5	60.3	18.7

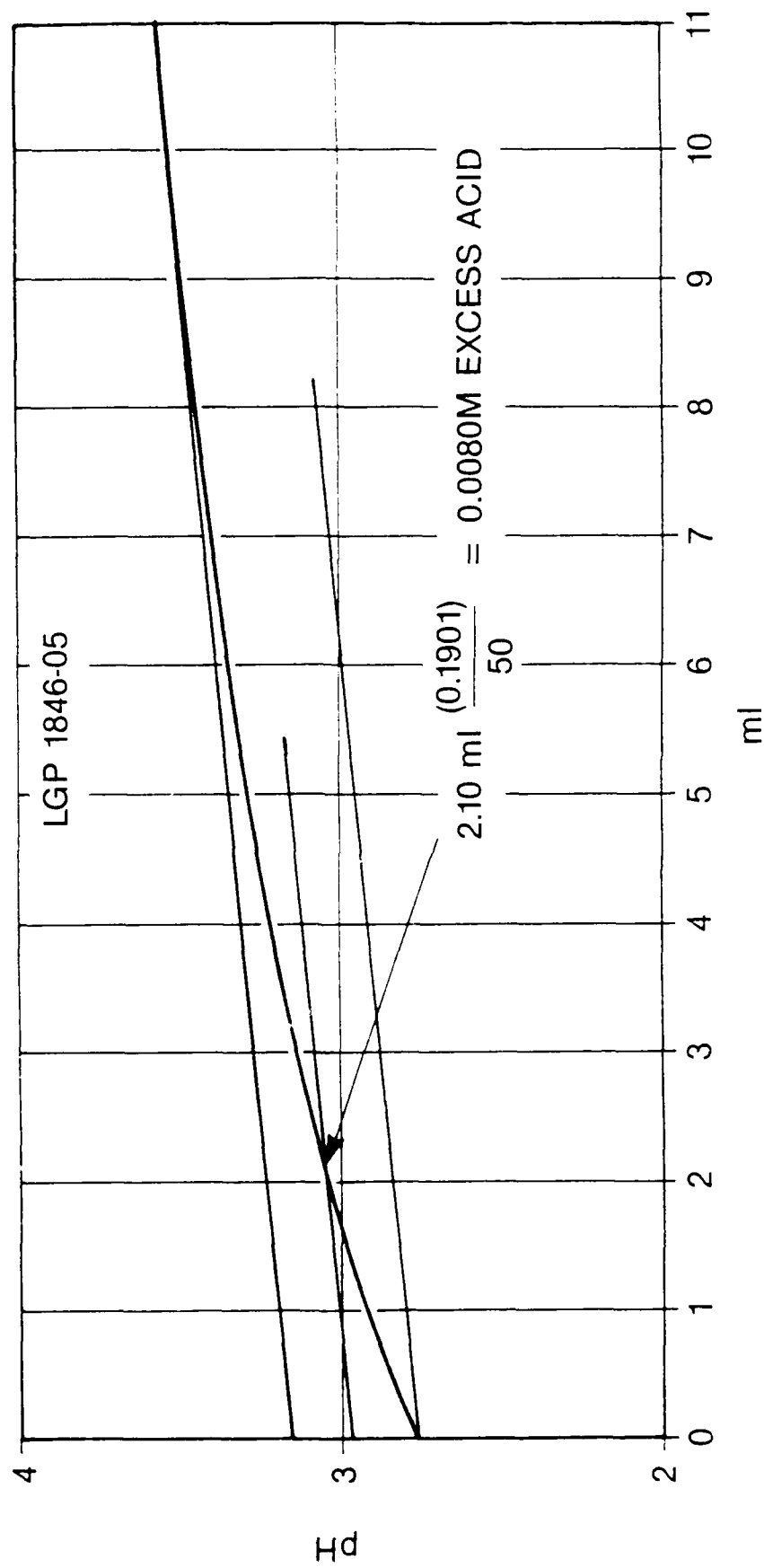
*Thiokol* CORPORATION, TACTICAL OPERATIONS, Elkton Division

# **ANALYSES OF LGP 1846 LOTS**

Lot	Total Moles Moles / 100 g	Total NO <sub>3</sub> Moles / 100 g	HAN/TEAN	Fe, ppm
-01	0.7279	0.7270	3.03	3
-02	0.7301	0.7258	3.20	1
-03	0.7279	0.7275	3.11	0.8
-04	0.7273	0.7234	3.16	0.7
-05	0.7245	0.7207	3.17	1.0
-06	0.7275	0.7220	3.13	1.4
-07	0.7249	0.7243	3.08	1.4
-08	0.7247	0.7249	3.11	1.6
<u>Target</u>				
Max		0.7288	3.28	<5
Min		0.7184	3.06	—

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# EXCESS ACID TITRATION IN LGP



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## METAL CONTAMINATION LEVEL

If HAN solution at 24% bw has 1 ppm Fe

$$\frac{1 \text{ g Fe}}{10^6 \text{ g soln}} \times \frac{100 \text{ g soln}}{24 \text{ g HAN}} = \frac{4.2 \text{ g Fe}}{10^6 \text{ g HAN}} = 4.2 \text{ ppm Fe}$$

Concentration of solution to 85% HAN

$$\text{yields } 4.2 \times 0.85 = 3.5 \text{ ppm Fe}$$

Use of this solution in LGP 1846 (60.8% HAN)

$$\text{yields } 4.2 \times 0.608 = 2.5 \text{ ppm Fe}$$

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**SUGGESTED LGP 1846 SPECIFICATIONS**

<b>Content:</b>	Total nitrate, moles / 100g	0.7236 ± 0.0052
	HAN / TEAN	3.17 ± 0.11
	H <sub>2</sub> O, %	20.0 ± 0.5
	HAN, %	60.8 ± 0.5
	TEAN, %	19.2 ± 0.5
	Metals, ppm	< 5 (transition metals) e.g., Fe, Ni, Cu, Pb, Sn
	Excess acid, M HNO <sub>3</sub>	<0.1
<b>Analyses:</b>	UV (302 nm)	
	Titration (aqueous / oxime)	
	Karl Fischer	
	AA	
<b>Packaging:</b>	Polyethylene (leached)	
	Tamper-proof closure	
	Vented closure (14.7 psig)	

*Thiokol* CORPORATION, TACTICAL OPERATIONS, Elkon Division

5th ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT  
US ARMY BALLISTIC RESEARCH LABORATORY  
ABERDEEN PROVING GROUND, MD  
22-24 AUG 89

Title of Paper Development of Analytical Methodology for Liquid Propellants

Presentation Time Request 20 (min)

Type of Paper: Progress; Summary; X State-of-art; Other

Speaker's Name Stan Griff Phone Number (201) 366-3609

Affiliation/address GEO-CENTERS, Hopatcong, N.J.

Co-author(s) name(s) Edward Turngren, William Seals

ABSTRACT (Use reverse side if necessary)

The defense community's commitment to evaluate liquid gun propellants as a potential replacement of solid propellants in the 105mm and 155mm guns has resulted in the necessity of wide ranging investigations. A necessity for acceptance is the ability to be stored for indefinite periods under specified field exposure conditions. The stability and therefore integrity of these propellants, after being stored for extended periods of time, is necessary in order to meet ballistic requirements. The long-term storage of liquid propellants is required to determine whether there is any instability; its cause; and if necessary, its prevention. Fail/safe criteria is not presently available for liquid propellants under long-term storage conditions and a methodology is being developed to establish this criteria.

Analytical methods have been developed to provide means to monitor these long-term storage studies. Techniques which were previously developed for this program were reviewed, and those applicable for this program were investigated. The investigation led, in some cases, to revise or to create new methods for analysis of major ingredients, contaminants and degradation products. The methods which were selected were tested in-depth, and with several, comparison studies were conducted.

In conclusion, a capability is available to monitor liquid propellants during storage. This will permit the establishment of kinetics, decomposition mechanisms and specifications as well as the ability to evaluate additives.

ABSTRACT DEADLINE: JUNE 15, 1989



# **DEVELOPMENT OF ANALYTICAL METHODOLOGY FOR SURVEILLANCE MONITORING OF LIQUID PROPELLANTS**

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**AUGUST 1989**

**TASK 1: PROVIDE ANALYTICAL METHODOLOGY FOR MONITORING LIQUID PROPELLANTS.**

- ESTABLISH AND IDENTIFY MAJOR AND MINOR CONSTITUENTS.
- DETERMINE RANGE FOR QUANTITATION.
- ESTABLISH ANALYTICAL TECHNIQUES

**TASK 2: DETERMINE PHYSICO-CHEMICAL CHARACTERISTICS NECESSARY FOR DATA PROJECTIONS.**

- EFFECT OF COMPONENTS AND CONTAMINANTS.
- RECOMMEND SPECIFICATIONS FOR LP.
- POSTULATE DECOMPOSITION MECHANISMS.
- ESTABLISH FLAGS FOR CONDITION OF LP.
- DETERMINE POTENTIAL FOR FIELD TEST KIT.

**TASK 3: ACCELERATED STABILITY, LONG-TERM STORAGE AND BALLISTICS STUDIES.**

- ACCELERATED LAB STABILITY STUDIES WITH LP 1846.
- EFFECT OF TEMPERATURE AND CONTAMINANTS.
  - AMBIENT TO 65°C.
  - SPIKED WITH NITRIC ACID - 0 TO 0.3%
  - SPIKED WITH IRON - 0 TO 4PPM.
  - SPIKED WITH INHIBITOR AND IRON.
- LONG-TERM STORAGE WITH NEAT LP 1846.
  - TEMPERATURE RANGE - AMBIENT TO 65°C.
  - TEMPERATURE CYCLING - AMBIENT TO 65°C
- BALLISTICS STUDIES.
  - RELATE CHANGES IN COMPOSITION WITH ACCELERATING RATE CALORIMETRY (ARC) AND BALLISTICS.

# LIQUID GUN PROPELLANT COMPOSITION

## LP1846

HYDROXYLAMMONIUM NITRATE (HAN)	61
TRIETHANOLAMMONIUM NITRATE (TEAN)	19
WATER	20

## POTENTIAL IMPURITIES AND CONTAMINANTS INCLUDE:

Ammonium nitrate (AN)	Ethanolammonium nitrate (EAN)
Metals	Diethanolammonium nitrate (DEAN)
Nitric acid	

## POTENTIAL DEGRADATION PRODUCTS INCLUDE:

Nitric acid	Nitrosoamines	Nitric oxide
Water	Nitramines	Hydrogen cyanide
Nitrogen dioxide	Morpholines	Ammonia
Nitrous oxide	Hydrazines	Hydrogen
Nitrogen		Oxygen
	Carbon dioxide	
	Carbon monoxide	

## Review of Analytical Monitoring Techniques

<u>Component</u>	<u>Available</u>	<u>Recommended</u>
HAN	Titration-adequate IC-more versatile	IC/SFC-sensitive to small variations
TEAN, AN EAN, DEAN	Titration-does not resolve IC-resolves all species	IC/SFC-sensitive to small variations
H <sub>2</sub> O	Titration	Titration-Karl Fisher
Nitric acid	Titration	Titration-NonAq
Metals	IC-fastest GPAA-reference Polarography-complex and time consuming	IC-all in one run TM+3 requires development GPAA-slower
Gas Phase degradation products	GC and MS	GC-Two column method MS-confirm
Liquid Phase degradation products	LC	LC/SFC-methods require development

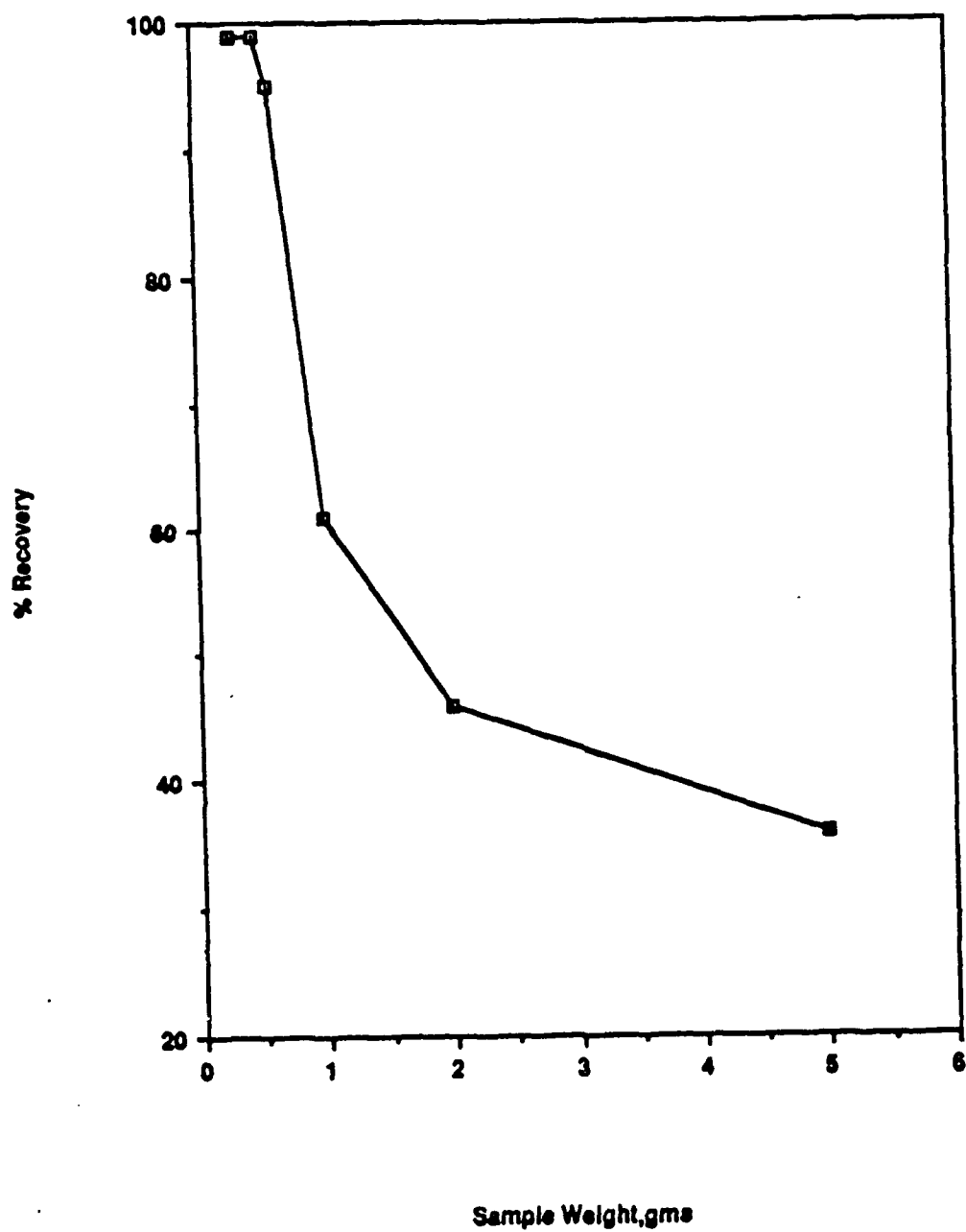
Note: Titration - Typical acid-base titrimetry.  
 IC - ion chromatography, ionic separation with a liquid eluant.  
 SFC - supercritical fluid chromatography, separation with supercritical carbon dioxide.  
 GPAA - graphite furnace atomic absorption spectrophotometry.  
 GC - gas chromatography, separation with a gaseous eluant.  
 LC - liquid chromatography, separation with a liquid eluant.  
 MS - mass spectrometry

## TITRATION SCHEME

1. **Free nitric acid:** LP in neat ethanol - 0.01N TBAH titrant.  
HAN and TEAN form single break after nitric acid break.
  
2. **HAN/TEAN:** LP in 100:1 ethanol/acetone - 0.2N TBAH titrant.  
Adequate sample for significant amount of titrant.  
Pre-addition of titrant to reduce titration time.  
HAN is HAN + free HNO<sub>3</sub>.  
TEAN is TEAN + weakly acidic impurities (AN, etc.).  
  

$$\begin{array}{ccc}
 \text{H}_3\text{NOHNO}_3 + \text{R}_2\text{C=O} & \text{---->} & \text{R}_2\text{C=NOH} + \text{HNO}_3 + \text{H}_2\text{O} \\
 \text{HAN} & & \text{OXIME}
 \end{array}$$
  
3. **2: Karl Fisher titration.**

# Nitric Acid Titration - % Recovery vs Sample Weight



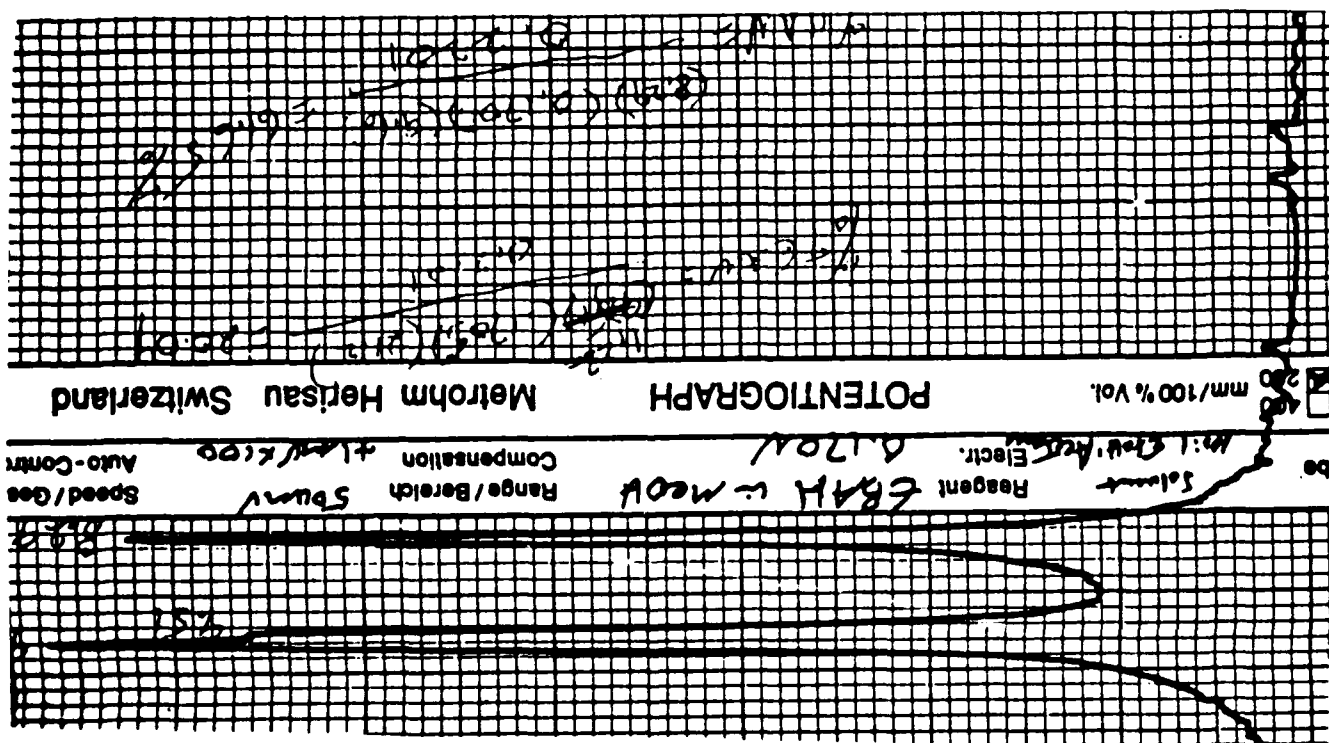
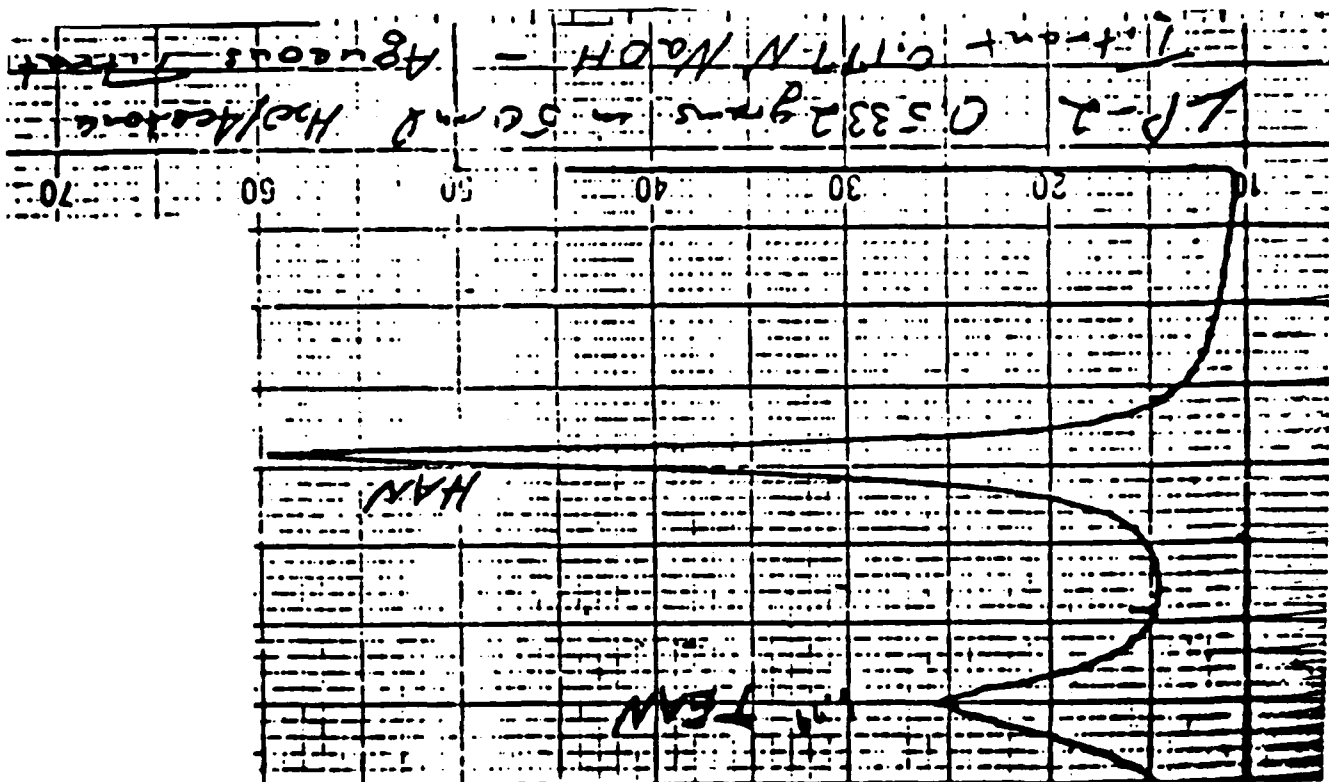
	Sample Wt,gms	% Recovery
1	0.3	99
2	0.5	99
3	0.6	95
4	1.0	61
5	2.0	46
6	5.0	36

## COMPARISON OF HAN TITRATION METHODS

<u>Sample</u>	<u>Non-Aqueous</u>		<u>Aqueous</u>
	<u>nBA</u>	<u>TBAH</u>	<u>NaOH</u>
LP 1846	59.02	59.70	58.65
LP-2	±0.04	±0.05	±0.02
LP 1846	60.04	59.40	58.78
LP-3	±0.01	±0.08	±0.06
HA·Cl		60.8	58.5

NOTE: HA·Cl, HCl, standards equivalent to 61.4% HAN.





## **SUMMARY OF LIQUID PROPELLANT TITRATIONS BY AQUEOUS AND NON-AQUEOUS TECHNIQUES**

### **NITRIC ACID:**

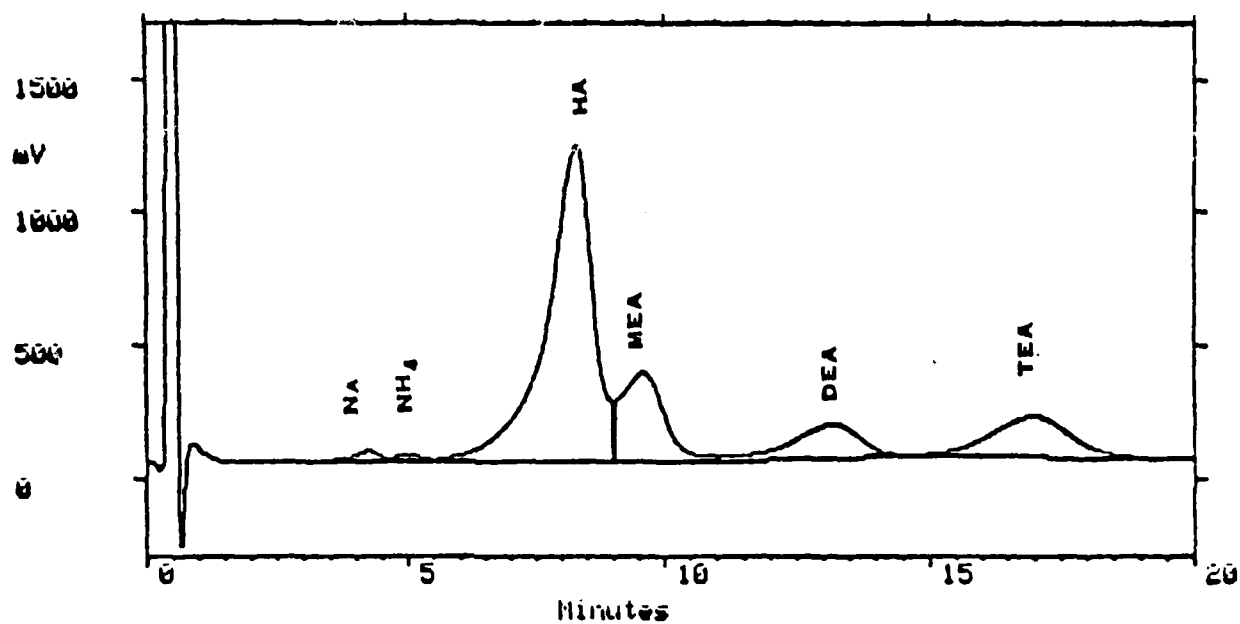
1. Both methods - show agreement.
2. Both methods - require dilute samples.
3. Non-aqueous - accurate and easily interpreted.
4. Safety directive - sample inventory reductions.
5. Environmental directive - reduction of wastes for disposal.
6. Non-aqueous - selected for nitric acid analysis.

### **HAN/TEAN:**

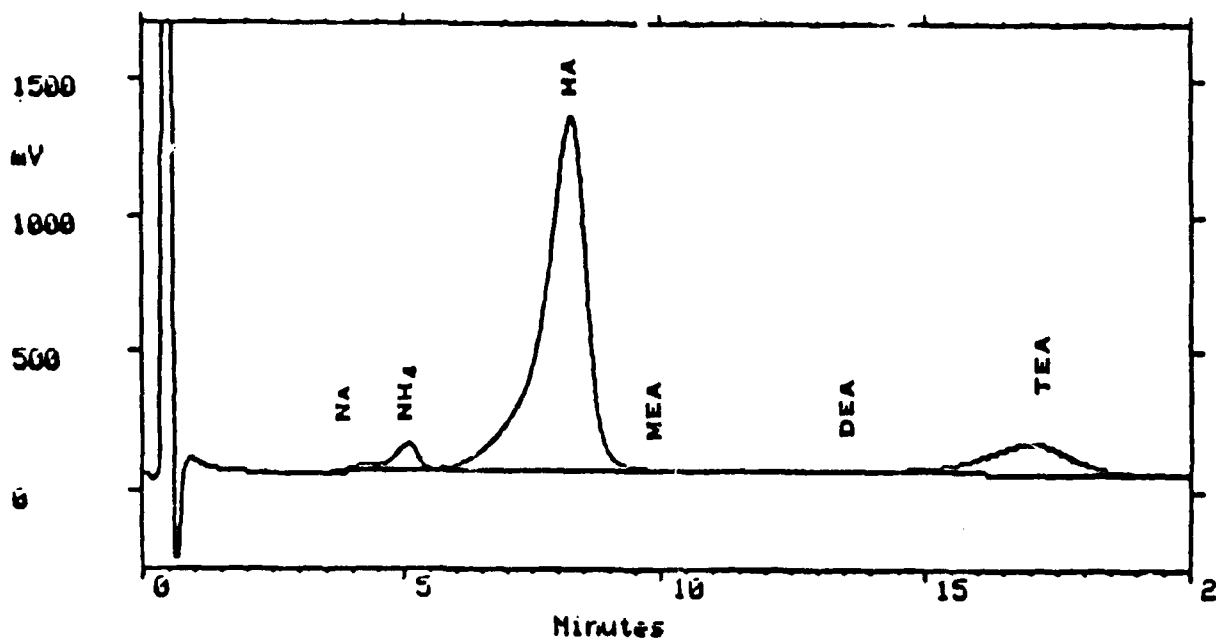
1. Non-aqueous - instantaneous conversion of HAN.
2. Non-aqueous - more precise and accurate.
3. Non-aqueous - detects TEAN and other weak acids.
4. Titrimetry - to be replaced by IC or SFC.

ION CHROMATOGRAPHY  
AMMONIUM CATION METHOD

Chromatogram of EASTD



Chromatogram of LP2



**Comparison of Graphite Furnace AA and ICP  
Metals Analyses of LP 1845 Lot# 1845-01-02**

<u>Metal</u>	<u>Perkin Elmer</u>	<u>ARL</u>
Fe	0.9ppm(ICP/ES)	1.0(ICP/ES)
Fe	1.8ppm(ICP/IS)	
Fe	1.9ppm(GPAA)	
Fe	1.5ppm(ICP/MS)	

**Note:**

IS = internal standard technique using scandium.

ES = external standard technique.

ICP = inductively coupled plasma. MS = ICP/MS.

GPAA = graphite furnace AA.

Dilution for GPAA was 1/100.

Dilutions for ICP PE = none; ARL = 1/9th.

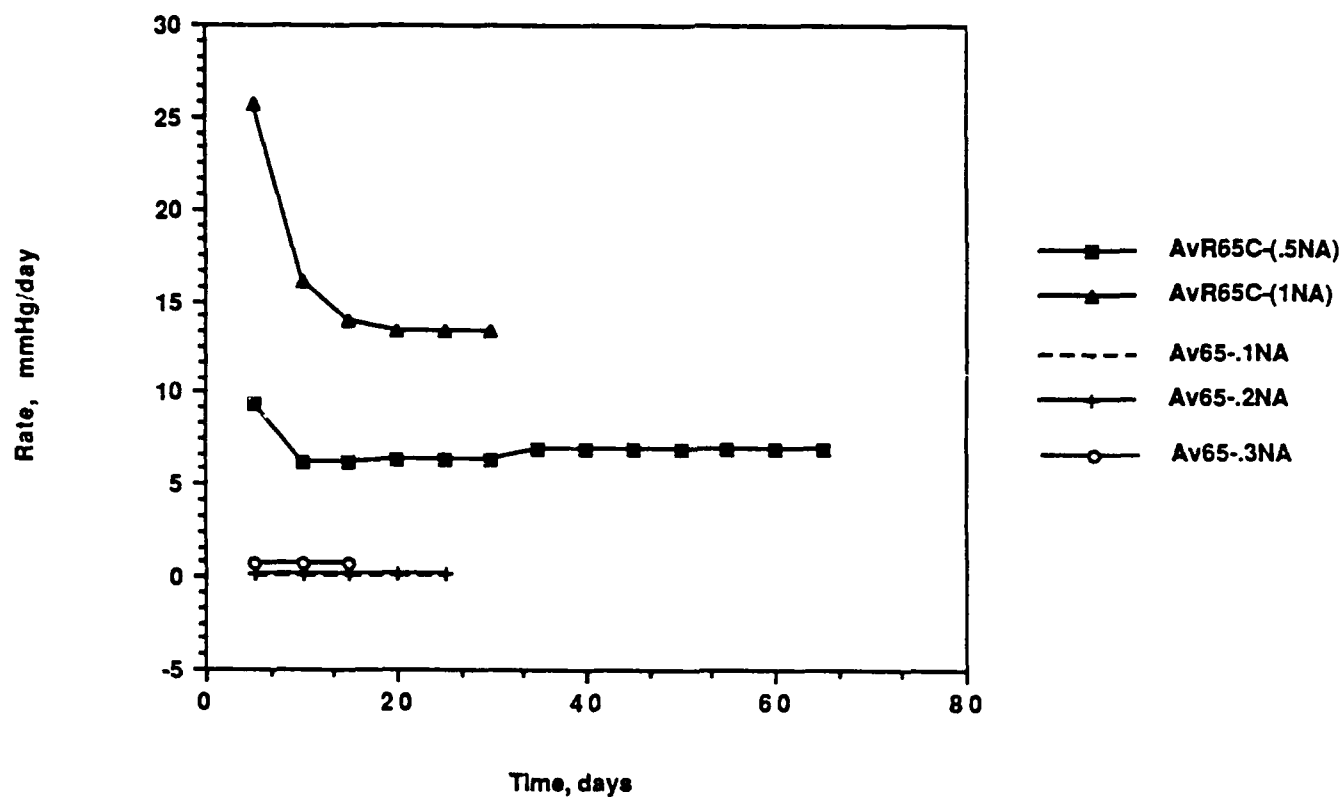
Same results obtained for Lot 292:

PE = 0.2ppm Fe (IS)      ARL = <0.01ppm Fe (ES)

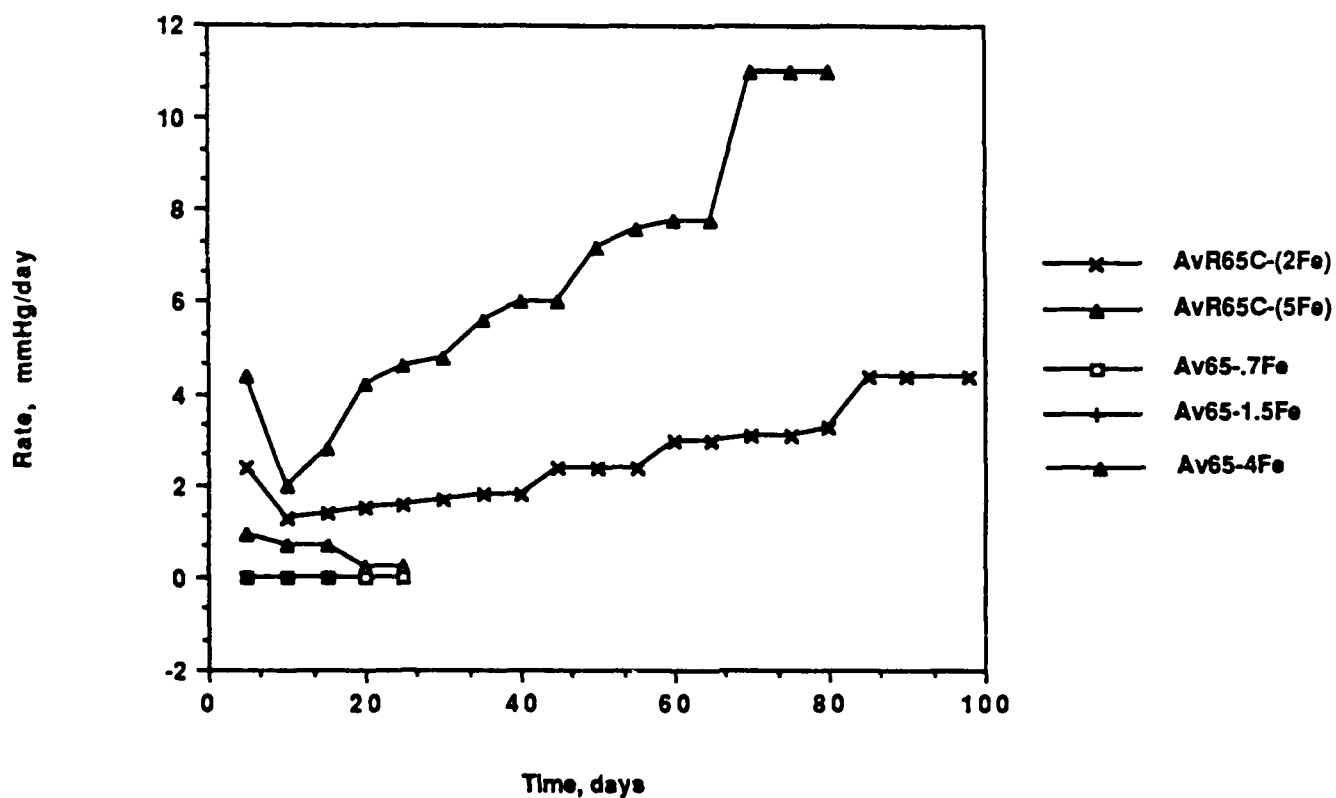
# LP 1846 PRESSURE-TIME STUDY INVENTORY

Sample Description	Temperature °C	Fe,ppm	Nitric Acid, %	Inhibitor Ratio, L:M
LP Neat	30	0.7	0.10	0
LP + acid		0.7	0.15	0
LP + acid		0.7	0.20	0
LP + iron		1.5	0.10	0
LP + iron		4.0	0.10	0
LP Neat	50	0.7	0.10	0
LP + acid		0.7	0.15	0
LP + acid		0.7	0.30	0
LP + iron		1.5	0.10	0
LP + iron		4.0	0.10	0
LP Neat	65	0.7	0.10	0
LP + acid		0.7	0.20	0
LP + acid		0.7	0.30	0
LP + iron		1.5	0.10	0
LP + iron		4.0	0.10	0
LP + inhibitor		0.7,4	0.10	2:1

Rate vs Time at 65°C - LP1846 + Nitric Acid



Rate vs Time at 65°C - LP1846 + Iron



## STATUS AND FUTURE PLANS

1. Preliminary analytical methodologies have been chosen.
  - a. IC - HAN, TEAN and AN.  
SFC - being investigated.
  - b. IC - transition metals.  
GPAA - reference for transition metals.
  - c. LC - liquid phase degradation products.  
SFC - being investigated.
  - d. Non-Aqueous Titration - nitric acid.
  - e. Accelerating Rate Calorimetry - to compliment ballistics.
2. Coordination of analyses between ARDEC, BRL, Olin, and Thiokol and formation of Analytical Working Group is being discussed.
3. Accelerated surveillance study has been initiated with "production quality" propellant.

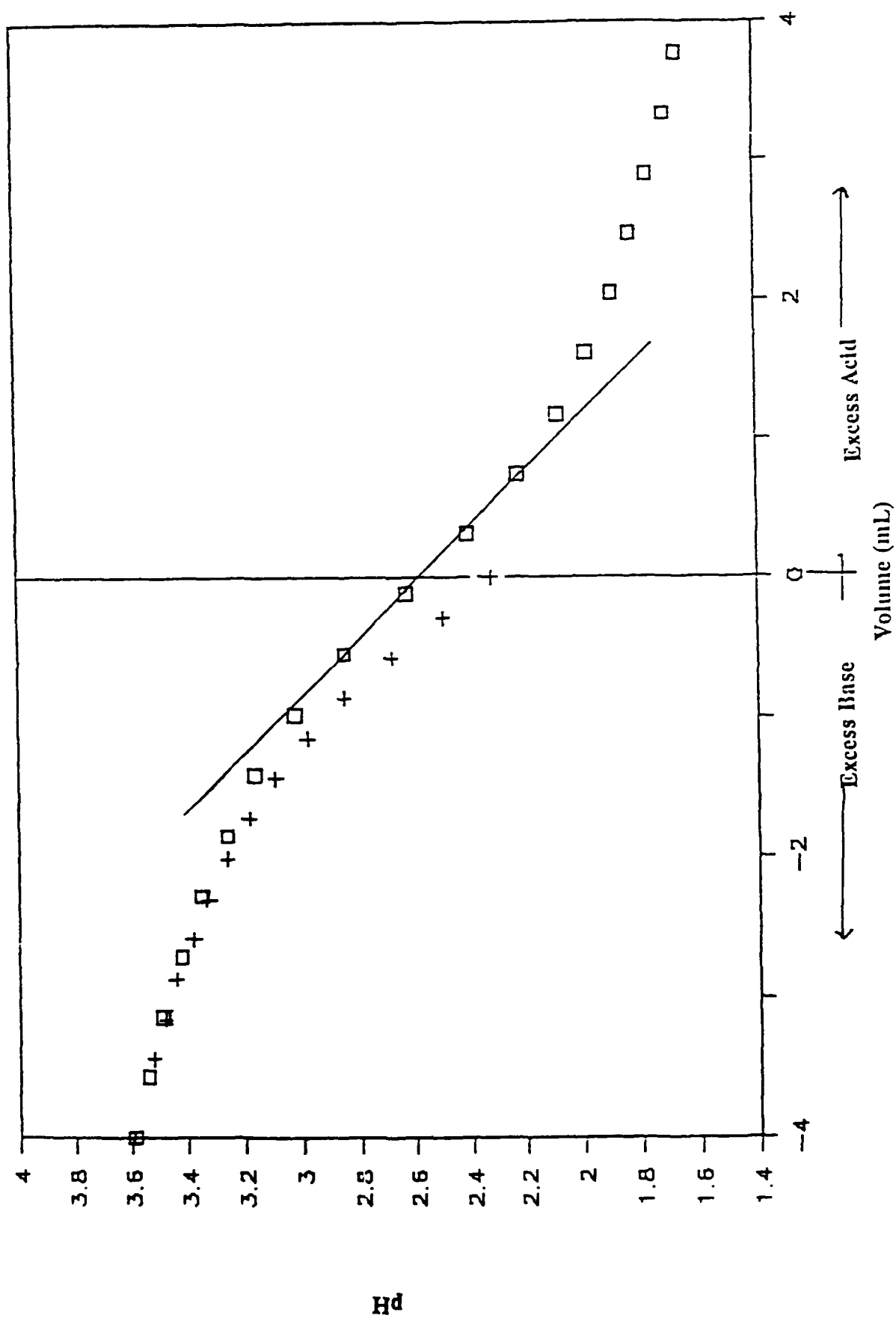
# MEASURING EXCESS $\text{HNO}_3$ IN LIQUID PROPELLANTS

- Titrating Neutral LP with 0.25N Base
- Back Titrating Basic Solution with 0.25N Acid
- Derivative Evaluation
- Further Computer Evaluation

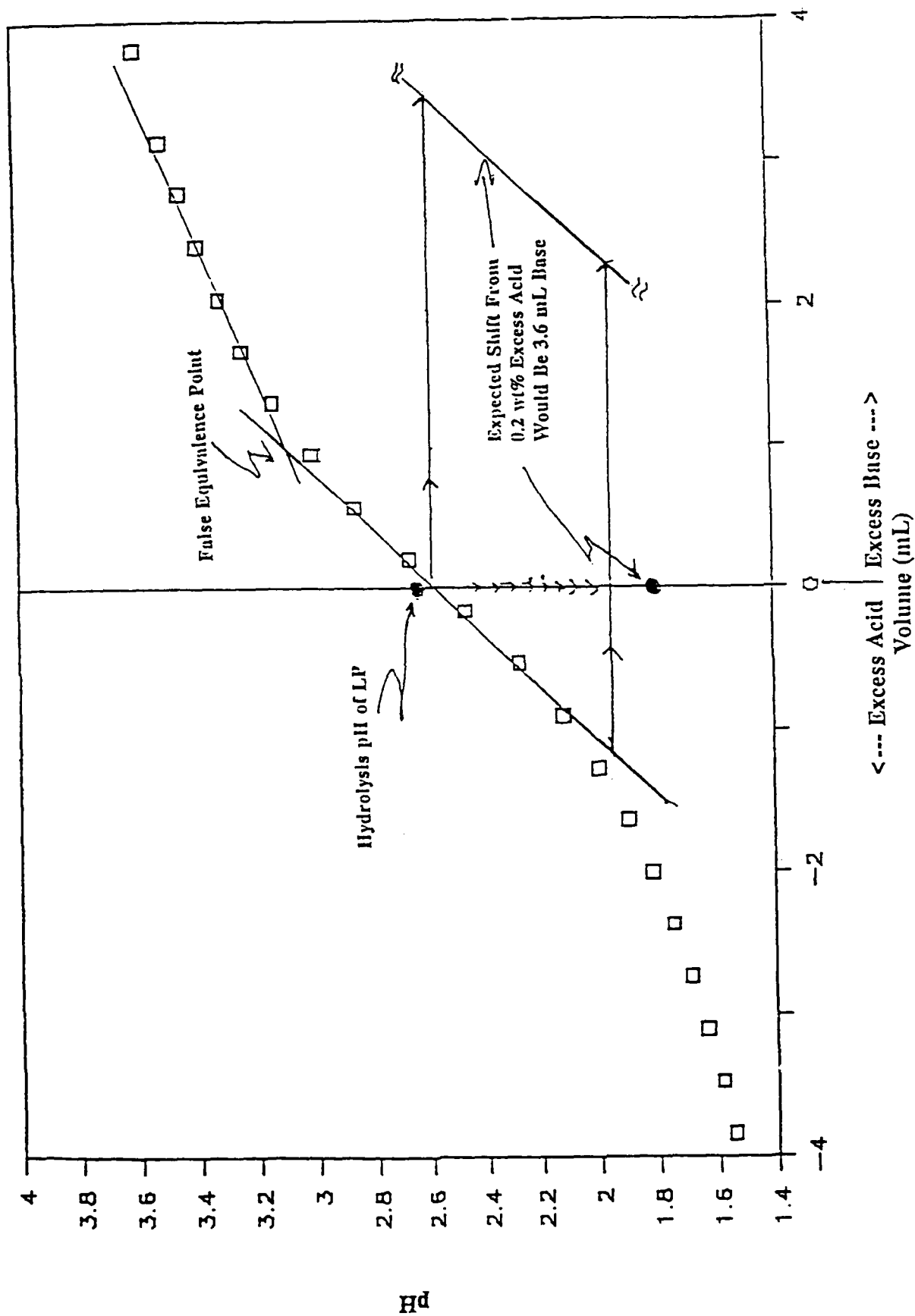
**CONCLUSION:** Proposed Analytical Method Measures Excess Acid, pH's and Derivatives That Are Compatible with Hydrolysis Constants.



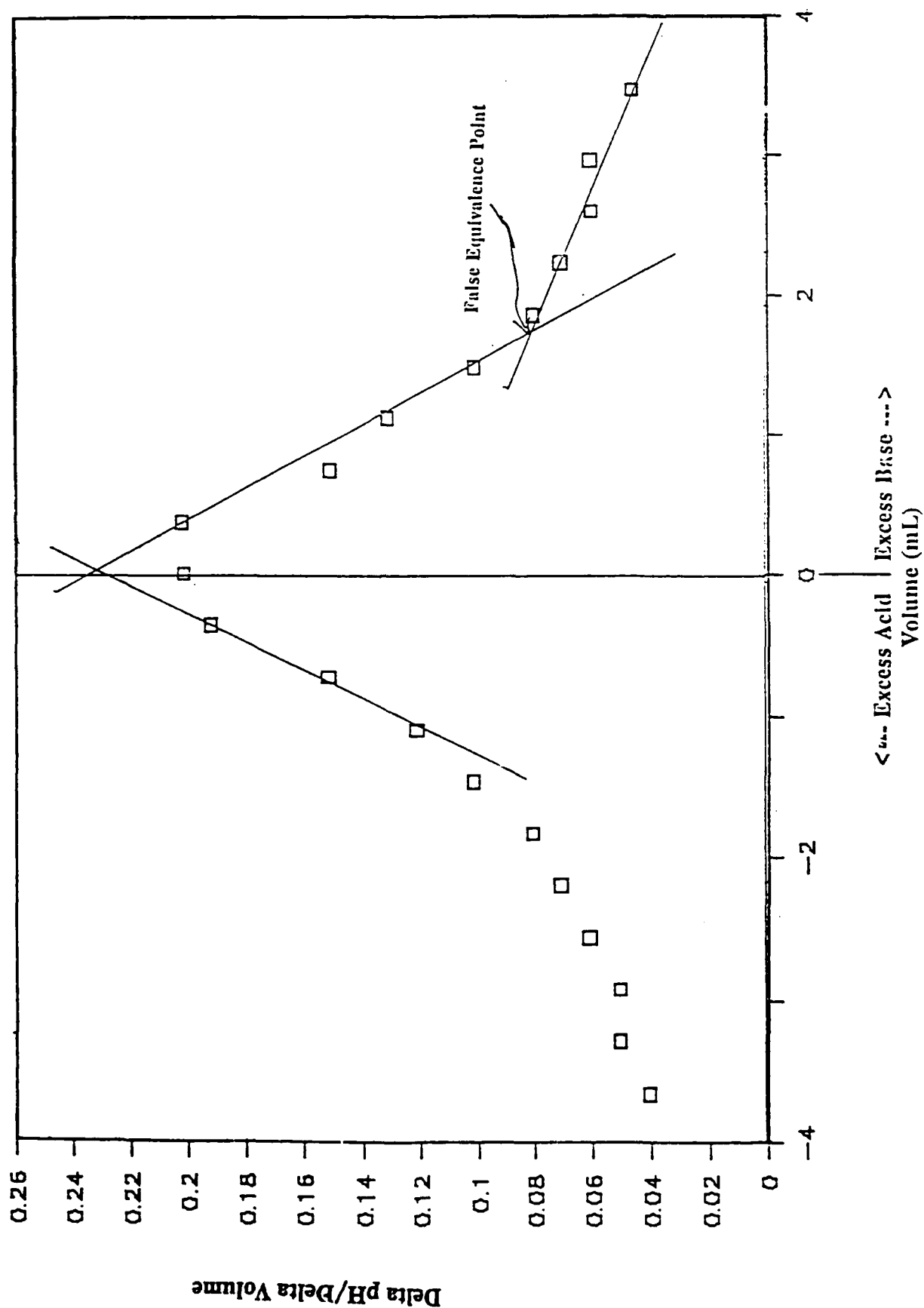
SYSTEM: 20 mL LP, 40 mL H<sub>2</sub>O,  
All Titrated with NaOH or HNO<sub>3</sub>



SYSTEM: 20 mL LP, 40 mL H<sub>2</sub>O, 4.0 mL Excess HNO<sub>3</sub>  
All Titrated with NaOH

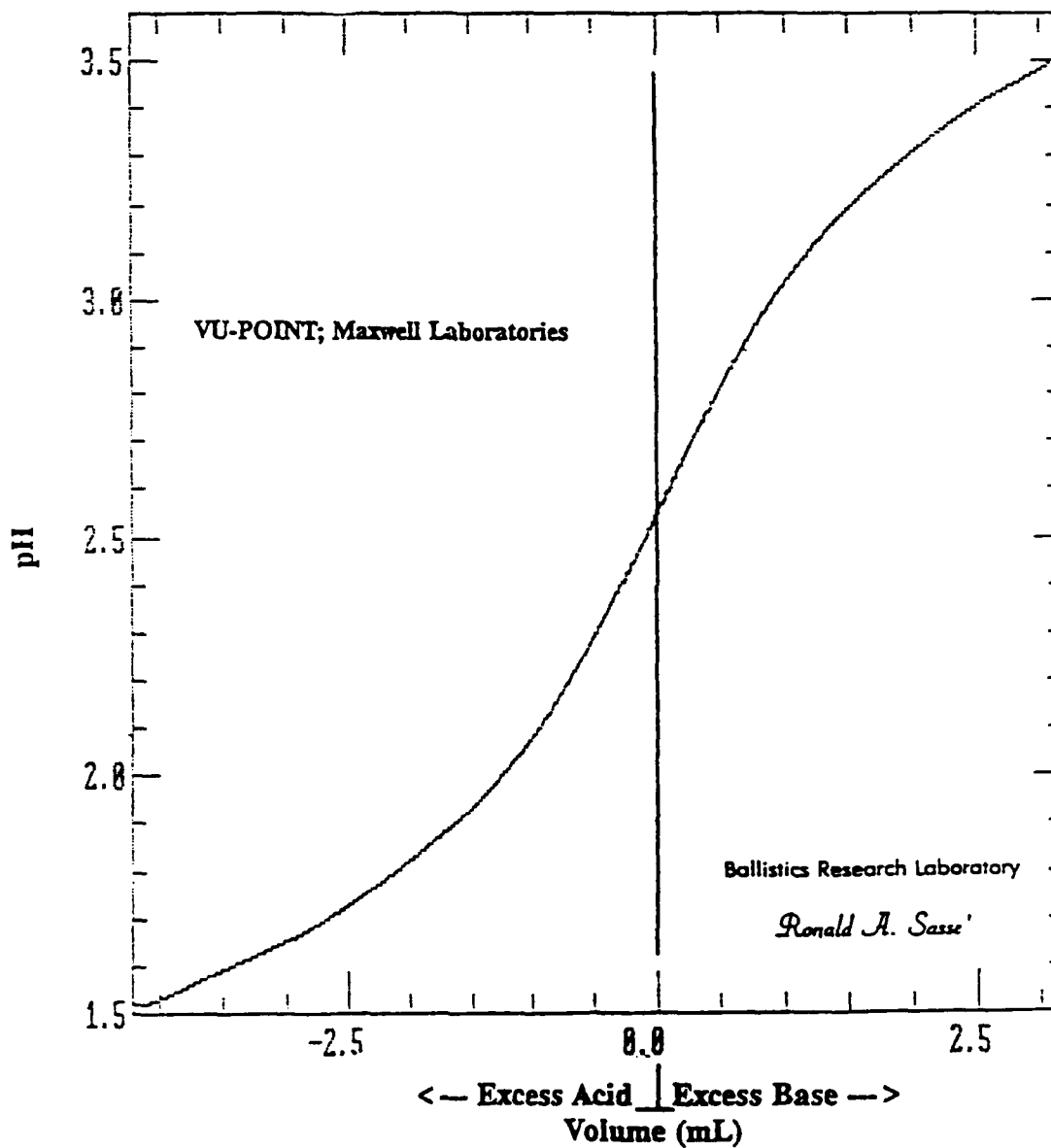


SYSTEM: 20 mL LP, 40 mL H<sub>2</sub>O, 4.0 mL Excess HNO<sub>3</sub>  
All Titrated with NaOH



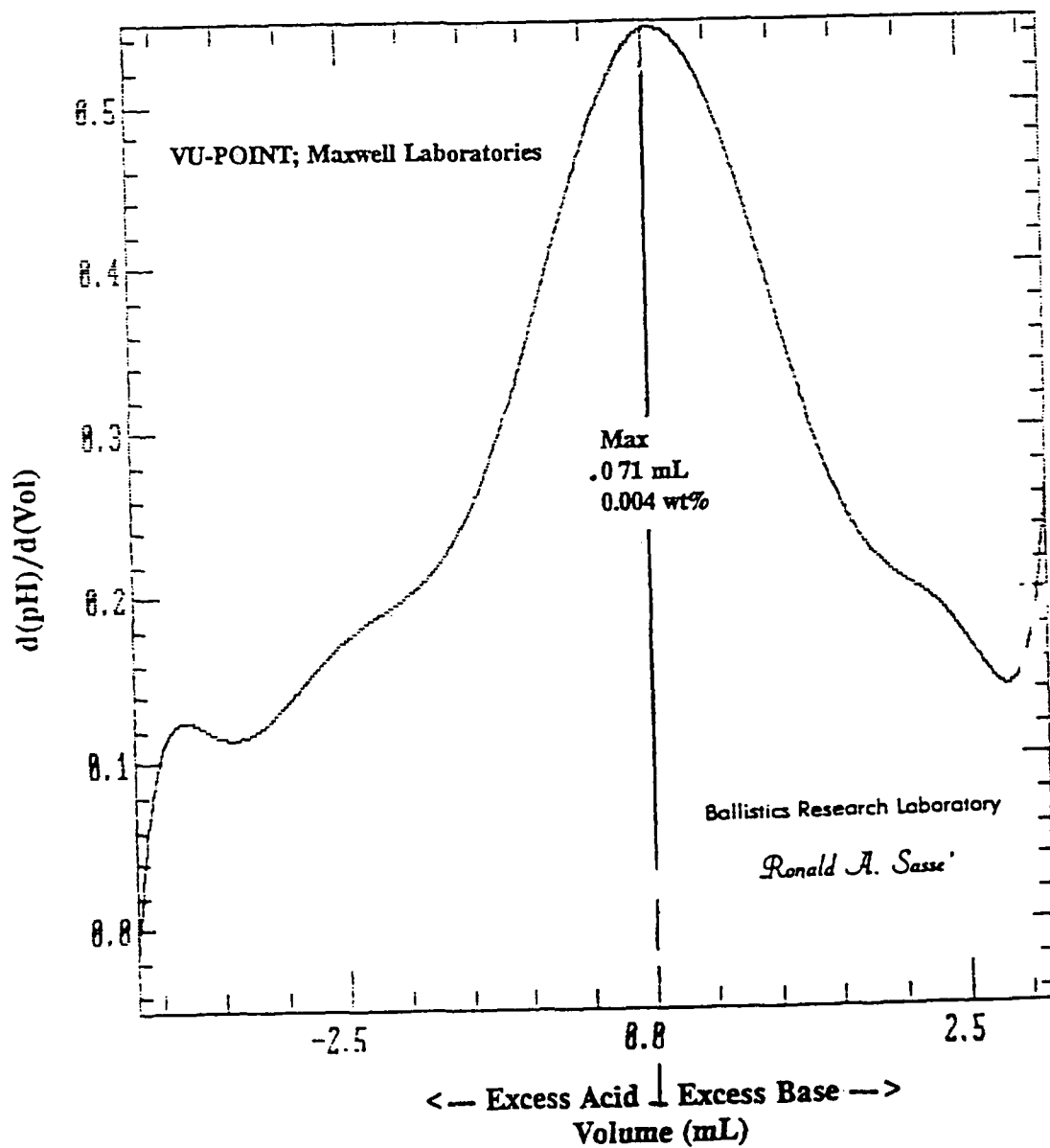
SYSTEM: 20 mL LP, 40 mL H<sub>2</sub>O, 4.0 mL Excess HNO<sub>3</sub>  
All Titrated with NaOH

Polynomial Fit, deg 10



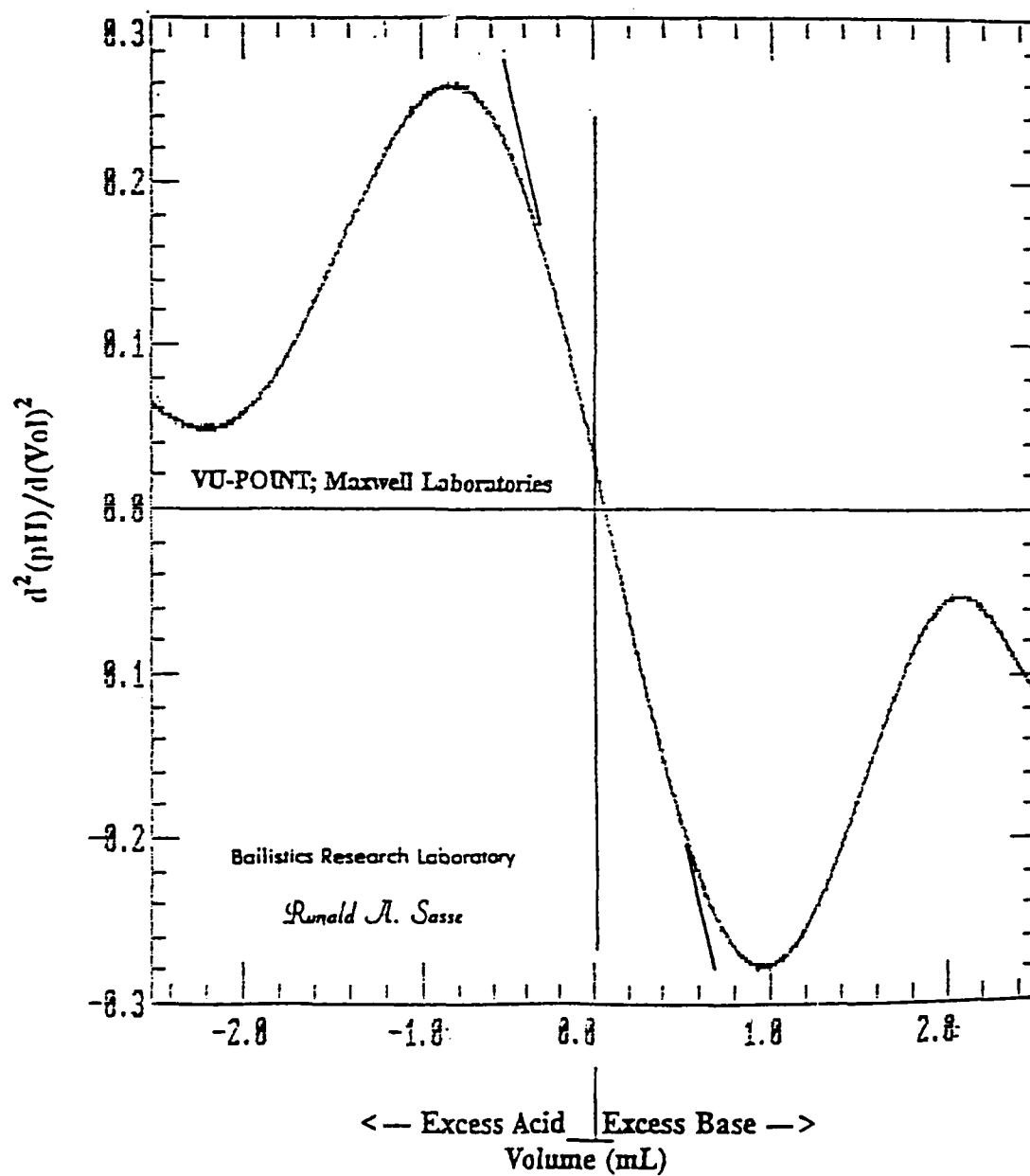
SYSTEM: 20 mL LP, 40 mL H<sub>2</sub>O, 4.0 mL Excess HNO<sub>3</sub>  
All Titrated with NaOH

Derivative of Polynomial



SYSTEM: 20 mL LP, 40 mL H<sub>2</sub>O, 4.0 mL Excess HNO<sub>3</sub>  
All Titrated with NaOH

Second Derivative of Polynomial



EXCESS STRONG ACID IN LIQUID PROPELLANTS

<u>DESCRIPTION SAMPLE LP</u>	<u>% STRONG ACID</u>	<u>DEV</u>	<u># SAMPLES</u>
1845-01	0.007		1
1845-01; 55	0.003	0.002	5
1845-290 M-T	0.295	0.000	3
1845-293 M-T	0.294	0.001	3
1846-01; 20 M-T	0.155		1
1846-02 NOS/IH	0.155	0.000	3
1846-02; 69	0.001	0.007	3
1846-03; 8	0.004	0.001	2
1846-03; 27	0.027		1
1846-04; 14	0.071		1
1846-05	-0.050	0.002	8
1846-06	0.001	0.003	5
1846-07; 67	-0.004	0.002	5
HAN; 2.8 M SW	0.075		1
HAN: 13 M #184	0.022	0.001	5
HAN; 13 M #851-27	0.006	0.001	5
HAN; 13 M #851-47	0.004	0.001	5
TEAN; 80% M-T 278	- 0.022	0.003	3

5th ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT  
US ARMY BALLISTIC RESEARCH LABORATORY  
ABERDEEN PROVING GROUND, MD  
22-24 AUG 89

Title of Paper Human Exposure and Occupational Health Surveillance of Liquid  
Gun Propellant (LGP) Workers  
Presentation Time Request 20 (min)  
Type of Paper: X Progress;        Summary;        State-of-art;        Other  
Speaker's Name MAJ David L. Parmer Phone Number (301) 663-7297  
Affiliation/address U.S. Army Biomedical Research and Development Laboratory,  
ATTN: SGRD-UBG-0, Fort Detrick, Frederick, MD 21701-5010  
Co-author(s) name(s) MAJ David A. Smart

ABSTRACT (Use reverse side if necessary)

Development of information on human exposure to LGP serves two basic purposes. In cases of documented over-exposure or accidental spill, human responses provide a basis for determining if toxicity data developed from animal studies accurately predict effects. Secondly, a routine surveillance program, particularly for a new compound, provides assurance that unexpected exposures will not occur. When the U.S. Army Biomedical Research and Development Laboratory (USABRDL) research program on such exposures began, all reported historical exposure situations were investigated to determine if legitimate information was available and suitable for defining effects. The reported exposure situations proved to be anecdotal and did not provide significant information on effects. One documented accidental exposure did occur after the USABRDL study program was initiated, but the supporting health clinic failed to follow proper procedures in conducting tests for systemic toxicity. The USABRDL enlisted cooperation from two ballistics research contractors in the conduct of a medical surveillance program. A third contractor is being solicited for inclusion in the program. Medical surveillance results will be discussed.

ABSTRACT DEADLINE: JUNE 15, 1989



# DESIGN OF LIQUID PROPELLANT MEDICAL SURVEILLANCE PROGRAM

- INITIAL PLAN WRITTEN IN 1984, ADOPTED BY GENERAL ELECTRIC  
IN 1986
  - ▲ KEY FEATURES INCLUDED
    - MEDICAL EXAM WITH EMPHASIS ON METHEMOGLOBIN MEASUREMENTS
    - PRECAUTIONS, PARTICULARLY WITH RESPECT TO PREVENTION  
OF SKIN CONTACT
    - TREATMENT RECOMMENDATIONS
- 1ST REVISION - 1988
  - ▲ INTERIM RESEARCH RESULTS INDICATING SIGNIFICANT ADVERSE  
EFFECTS FOLLOWING SKIN EXPOSURE LEAD TO ADDITIONAL  
RECOMMENDATIONS FOR PROTECTION AGAINST ACCIDENTAL  
SPILLAGE AND RECOMMENDATIONS CONCERNING MEDICAL  
TREATMENT
- PROPOSED REVISIONS UNDER REVIEW
  - ▲ RELATING METHEMOGLOBIN MEASUREMENTS TO PERIOD OF EXPOSURE
  - ▲ IMPROVED METHEMOGLOBIN PROCEDURES

## IMPLEMENTATION - VOLUNTARY INDUSTRY PROGRAMS

### ●GENERAL ELECTRIC - INITIATED 1986

#### ▲FIRST REPORT NOV 1987

- BASELINE ON INDIVIDUALS ESTABLISHED
- NO UNUSUAL FINDINGS FROM ROUTINE SURVEILLANCE
- REPORT OF INCIDENT INVOLVING 3 INDIVIDUALS, NO EXPOSURES

#### ▲SECOND REPORT APRIL 1989

- NO UNUSUAL FINDINGS FROM ROUTINE SURVEILLANCE
- GE PHYSICIAN TO INITIATE METHEMOGLOBIN MEASUREMENTS FOLLOWING WORK PERIODS

### ●OLIN INITIAL PROGRAM - APRIL 1987

#### ▲FIRST REPORT APRIL 1988

- BASELINE ON INDIVIDUALS ESTABLISHED
- FURTHER ACTION BEING PLANNED FOR OPERATIONS AT CHARLESTON, TN

# REQUIREMENTS AND OBJECTIVES FOR MEDICAL SURVEILLANCE OF LIQUID GUN PROPELLANT EXPOSED WORKERS

## • MEDICAL RESEARCH PLAN FOR LGP

### ▲ REQUIREMENTS

- COMPLY WITH TOXIC SUBSTANCES CONTROL ACT FOR  
NEW CHEMICALS
- COMPLY WITH OCCUPATIONAL SAFETY AND HEALTH  
ACT FOR WORKER EXPOSURE TO CHEMICALS
- COMPLY WITH ARMY REGULATIONS ON HEALTH HAZARD  
ASSESSMENT AND MANPRINT

●MEDICAL RESEARCH PLAN (CONT.)

▲OBJECTIVES

- DOCUMENT PREVIOUS HUMAN EXPOSURE
- DESIGN MEDICAL SURVEILLANCE, EMERGENCY TREATMENT AND PROSPECTIVE EPIDEMIOLOGY PROTOCOLS
- CONDUCT ANIMAL TOXICOLOGY
- CONSTRUCT HUMAN EXPOSURE SCENARIOS FOR AN LP - BASED GUN SYSTEM
- DEFINE ADDITIONAL STUDIES REQUIRED TO FIELD THE WEAPONS SYSTEM

●MEDICAL SURVEILLANCE OBJECTIVES

- ▲PROTECT WORKERS, PARTICULARLY AS NEW INFORMATION BECOMES AVAILABLE
- ▲EVALUATE EFFECTIVENESS OF MEDICAL SURVEILLANCE, EMERGENCY TREATMENT AND WORKER PROTECTION PRACTICES
- ▲PROPERLY DOCUMENT HUMAN RESPONSES FROM ACCIDENTAL EXPOSURES

## IMPLEMENTATION - MILITARY PROGRAMS

- BALLISTICS RESEARCH LAB COORDINATED SURVEILLANCE GUIDELINES WITH THE ABERDEEN CLINIC IN 1985
- THE OFFICE OF THE SURGEON GENERAL REQUESTED THAT HEALTH SERVICES COMMAND COORDINATE REVISED PLAN WITH THE NAVY, WATERVLIET, PICATINNEY, APG, AND FT. BELVOIR IN 1989

5th ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT  
US ARMY BALLISTIC RESEARCH LABORATORY  
ABERDEEN PROVING GROUND, MD  
22-24 AUG 89

Title of Paper: An Overview of Chemical and Biological Processes  
Which May Lead to Degradation of HAN and TEAN in  
the Environment

Presentation Time Request: 20 (min)

Type of Paper: X Progress;      Summary;      State-of-art;      Other

Speaker's Name: Dr. M. L. Taylor Phone Number: (513) 782 4700

Affiliation/address: PEI Associates, Inc., 11499 Chester Road,  
Cincinnati, Ohio 45246

Co-author(s) name(s): M.A. Dosani (PEI), and C. Graham (USATHAMA)

**ABSTRACT**

A liquid propellant, currently being developed, consists of a mixture of an oxidizer, hydroxylammonium nitrate (HAN), a fuel, triethanolammonium nitrate (TEAN), and water. TEAN has been found to contain a hazardous impurity, N-nitrosodiethanolamine (NDELA) which is a carcinogen and poses an exposure hazard to personnel manufacturing the TEAN. The purpose of this project is to provide U. S. Army Toxic and Hazardous Materials Agency (USATHAMA) with a listing of potential methods for demilitarizing and disposing of the HAN-TEAN propellant residues which, on the basis of engineering, environmental and cost considerations, appear to be feasible. In addition, methods for performing bench-scale evaluation and concepts for full-scale implementation of these potential methods will also be recommended.

A comprehensive literature search has been performed in which information regarding the chemical/physical characteristics, as well as degradation and disposal processes for the HAN-TEAN propellants and formation of NDELA was sought. The major problem encountered at the outset of these investigations was the absence of published literature concerned directly with disposal or degradation of these propellant components as interest in these compounds is relatively new. Therefore, we searched for methods of disposing of similar compounds such as, triethanolamine, ammonium nitrate, and certain cutting fluids.

On the basis of the literature search results, we have identified thermal destruction and microbial degradation to be potentially applicable techniques for degrading the liquid

propellant. Thermal destruction has been used by the propellant manufacturer, however, this approach is not amenable to broad-scale and cost-effective use in numerous locations, some of which are quite remote.

As far as microbial degradation is concerned, we have identified techniques which entail aerobic/anaerobic biodegradation performed either in a bioreactor or in situ. Microbial degradation methods are currently being used for the disposal of various organic compounds and these processes are gaining wide acceptance. Currently, we are in the process of evaluating various types of microbial degradation techniques and assessing their potential for degrading the HAN-based liquid propellant.

Once the most promising disposal method is identified, the potential environmental impact of the selected technique will be evaluated. In addition, domestic and foreign environmental regulations will be reviewed to ensure that the selected disposal activities comply with the pertinent environmental statutes.

**SELECTION AND CONDUCT OF HAZARDS CLASSIFICATION  
TESTS FOR HAN-BASED LIQUID PROPELLANTS**

William R. Herrera  
Southwest Research Institute  
San Antonio, Texas  
(512) 522-3622

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ARDEC  
Picatinny Arsenal, New Jersey  
(201) 724-5378

Contract: DAAA21-88-D-0021

Test requirements relevant to establishing the hazards classification of solid and liquid energetic materials have been reviewed. Procedures for the classification of liquid materials have not been established in the Defense Hazard Classification Bulletin TB 700-2. This bulletin clearly states that it applies to energetic materials other than liquids. However, the bulletin has been used as a guide in the selection and conduct of recommended hazards classification tests for HAN-based liquid propellants.



## BACKGROUND

Hazards classification is the assignment of a hazards class to a material or end item. The guidelines and criteria used to make a hazards class selection requires a hazards classification procedure. At the present time, there is no normalized protocol for a hazards classification for liquid propellants. The current guide for a DOD hazards classification is the TB 700-2 manual.<sup>1</sup> This manual only provides the classification procedures for the storage and transport of solid propellants and explosives. From historical data on the cause of detonations and explosions of solid propellants and explosives, the major stimuli for initiating a reaction are the following: friction, impact, thermal, adiabatic compression, electrostatic discharge, and impingement. Figure 1 provides a schematic flow for establishing test criteria. The designated test requirements and specifications which appear in TB 700-2 had to be modified to accommodate a liquid instead of a solid test sample.

## TEST SELECTION AND SPECIAL CONSIDERATIONS

Southwest Research Institute under contract with the U.S. Army Armament, Munitions, and Chemical Command (AMCCOM, Picatinny Arsenal) selected and conducted a number of hazards classification tests on liquid gun propellants LP 1845 and LP 1846. The tests were consistent with those appearing in TB 700-2 Sample Summary Data Sheet presented in Figure 2. The following tests were conducted: detonation, ignition and unconfined burning, thermal stability, card gap, and impact sensitivity. The test procedures had to be modified to accommodate a liquid sample consisting of the following approximate compositions:

<u>LP 1845 (%)</u>	<u>Constituent</u>	<u>LP 1846 (%)</u>
63	Hydroxylammonium nitrate	60
20	Triethanolammonium nitrate	20
17	Water	20

Emphasis was placed on eliminating all possible source of metal (such as iron, copper, nickel, transition metal per se) contamination. This was done because of the liquid propellant becomes sensitized and are subject to degradation when contaminated with metal salts. The use of 316 series stainless steel and polyethylene containers was stressed. The stainless steel containers were passivated with nitric acid followed by thorough rinsing with deionized water to eliminate possible contamination. The polyethylene containers were immersed in boiling deionized water to eliminate possible organic and inorganic contaminants.

## TEST SPECIFICATIONS

A brief description of requirements for the individual tests follows.

### *Detonation Test*

This test involves placing a solid lead cylinder (1.5 inches in diameter and 4 inches high) on a 0.5-inch thick 12-inch square mild steel plate. A No. 8 blasting cap is placed perpendicular to and in contact with a flat surface of a 2-inch cube sample of the propellant

- 
1. TB 700-2 (Army designation), Department of Defense Explosives Hazard Classification Procedures, September 1982.

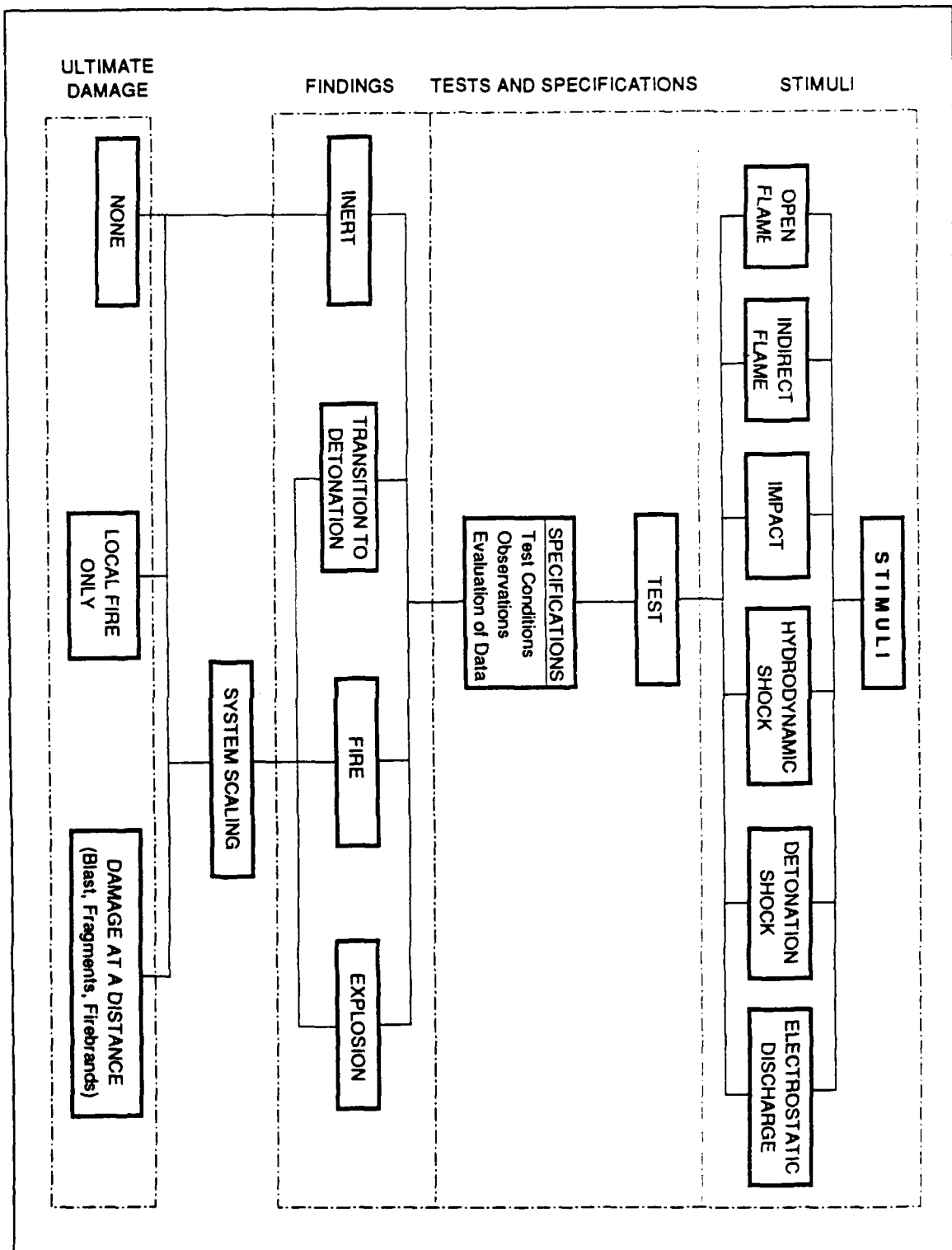


Figure 1. Hazard Classification Test Criteria

TB 700-2  
NAVSEAINST 8020.8  
TO 11A-1-47  
DLAR 8220.1

# SUMMARY DATA SHEET

Date \_\_\_\_\_

Sponsoring Agency \_\_\_\_\_

Contract No. \_\_\_\_\_

## Explosive or Propellant Identity (Type No.)

Spec. \_\_\_\_\_ Batch \_\_\_\_\_

Mfg. Date \_\_\_\_\_

### Detonation Test<sup>1</sup>

		Detonated		Burned		Fragmented	
		Yes	No	Yes	No	Yes	No
No. 8 Blasting Cap	Test I	—	—	—	—	—	—
	Test II	—	—	—	—	—	—
	Test III	—	—	—	—	—	—
	Test IV	—	—	—	—	—	—
	Test V	—	—	—	—	—	—

Samples: Five 2-inch cubes.

Test: One blasting cap per sample.

### Ignition and Unconfined Burning Test<sup>1</sup>

	Exploded	Average Burning Time
	Yes No	Seconds
One 2-inch cube	— —	—
One 2-inch cube	— —	—
Four 2-inch cubes	— —	—

Samples: Six 2-inch cubes.

### Thermal Stability<sup>1</sup>

Test: 48 hours at 75°C in vented oven

Reaction \_\_\_\_\_

### Card Gap Test

50% value \_\_\_\_\_ (no. of cards)

Comment

No detonation with 0 cards

### Impact Sensitivity Test

Bureau of Explosives Impact Apparatus

Ten 3-3/4" (±1/16") Drop Test			Ten 10" (±1/16") Drop Test		
10 Trails			10 Trails		
Number of Trails Exhibiting			Number of Trails Exhibiting		
Explosion	Decomposition	No Reaction	Explosion	Decomposition	No Reaction
Flame and	Smoke	No Smoke	Flame and	Smoke	No Smoke
Noise	No Noise	No Noise	Noise	No Noise	No Noise

### APPROVED:

Test Director \_\_\_\_\_ Test Department Head \_\_\_\_\_

#### ASSIGNED CLASSIFICATION

DOT Forbidden
DOT Restricted*
DOT Class A
DOT Class B
DOT Class C
UN Number

DOD Approval (see Para 3-2)

Signature \_\_\_\_\_

Title \_\_\_\_\_

Organization \_\_\_\_\_

\* Shipping instructions are to be requested from DOT.

1. All tests conducted using a 2" diameter polyethylene bottle filled with 8 cubic inches of LGP.

Figure 2. Summary Data Sheet

which is then placed on top of the lead cylinder. A 2-inch diameter wood block with a hole drilled in its center may be used to position the blasting cap. Deformation of the lead cylinder 1/8 inch or more will be considered as evidence of a detonation. This test is conducted a minimum of five times or until a detonation occurs, whichever is the least number of tests. Two-inch diameter polyethylene bottles containing 8 cubic inches (131 cubic centimeters) of liquid propellant were used for these tests. The blasting cap was placed in a polyethylene bag to avoid contact of the metal sleeve with the liquid.

### ***Ignition and Unconfined Burning***

This test involves placing a 2-inch cube sample of the propellant on a bed of kerosene-soaked sawdust and igniting the sawdust with an electric matchhead ignitor. This test is repeated once for each propellant. Two-inch diameter capped polyethylene bottles containing 8 cubic inches (131 cubic centimeters) of liquid propellant were used for these tests. The test is repeated using four 2-inch containers end-to-end in a single row on a bed of kerosene-soaked sawdust.

### ***Thermal Stability Test***

This test requires that a 2-inch cube sample be placed in a constant temperature, explosion-proof oven. The temperature in the oven is then raised to 75°C and maintained at that temperature for 48 hours. The temperature is continuously recorded and the results of the test recorded. Two-inch diameter capped polyethylene bottles containing 8 cubic inches (132 cubic centimeters) of liquid propellant were used for these tests.

### ***Card Gap Test***

This test consists of supporting a witness plate on two edges parallel to and approximately 6 inches above the ground surface. The liquid propellant was placed in a section of mild steel tubing 1.875 inch OD and 0.219 inch thick and 5.5 inches long which was lined with 0.0015-inch polyethylene film and centered above the witness plate. Four small pieces of plastic 1/16 inch  $\times$  1/2 inch were used to support the tube containing the liquid propellant and to maintain a 1/16 inch air gap between the test sample and the witness plate. The air gap between the witness plate and the liquid propellant tube should be free of solid material. The pentolite booster is then placed on top of and in contact with test sample at the top of the tube and the E-99 blasting cap attached. If detonation does occur, then a series of tests using the same procedures as those identified above are repeated utilizing the attenuation cards. The attenuation cards are 0.01-inch cellulose acetate sheets or cards which are placed between the liquid propellant tube and the pentolite boosters. The first test is performed using eight cards and if a detonation occurs, then the number of cards is doubled for the second test. If no detonation occurs, the number of cards is halved. Doubling the number of cards is continued until no detonation occurs. When the number of cards is reached that prevents detonation, the next test is conducted with the number of cards reduced by half the preceding increment of increase (i.e., if detonation occurs at 32 cards but not at 64 cards, then the next test is run with 48 cards). If detonation occurs at the reduced number of cards (48 cards in the example cited above), the number of cards is increased by one-half the preceding increment (i.e., from 48 cards to 56 cards). This procedure is followed until the 50% probability of detonation is achieved.

### ***Impact Sensitivity Test***

This test can be performed on a liquid with a standard impact apparatus. The liquid test sample (0.03 cubic centimeters) is enclosed in a cavity formed by a steel cup, an elastic ring, and a steel diaphragm. A piston rests on the diaphragm and contains a vent hole which is blocked by the steel diaphragm. A 2-kg weight is dropped onto the piston. A positive result is indicated by puncture of the steel diaphragm accompanied by a loud noise or severe deformation of the diaphragm and evidence that the sample was completely consumed. Data are reported as the height which yields a 50% probability of initiation.

A summary of the test specifications that had to be modified to accommodate a liquid sample is presented in Figure 2.

### **TEST RESULTS AND INTERPRETATION**

Results of the tests listed above would be interpreted as follows.

#### ***DOT Designation***

Forbidden: If thermal stability test results in a detonation, burning, or marked decomposition of the sample.

Restricted: Compositions with an explosive impact sensitivity of less than 4 inches of drop height.

#### ***DOT Class A (DOD Class/Division 1.1)***

If one or more of the following occurs:

1. Detonation test resulted in an explosion (lead cylinder deformation of 1/8 inch or more).
2. Card gap tests have determined a detonation sensitivity of 70 or more cards.
3. Impact sensitivity test produces an explosion at drop heights between 4 inches and 10 inches using a 2-kg drop height.
4. Ignition and unconfined burning test produces a detonation.
5. Thermal stability test results in an explosion.

#### ***DOT Class B (DOD Class/Division 1.3)***

If one or more of the following occurs:

1. Detonation test results do not deform the lead cylinder more than 1/8 inch.
2. Card gap test does not detonate and indicates a detonation sensitivity value of less than 70 cards or no reaction at 0 cards.

3. Impact sensitivity test does not result in an explosion at drop heights of 10 inches or less.
4. Ignition and unconfined burning test results in a burning deflagration.
5. Thermal stability test does not result in an explosion, burning, or marked decomposition.

***DOT Class C (DOD Class/Division 1.4)***

- This class (division) comprises items which are primarily a moderate fire hazard.
- They will not contribute excessively to a fire.
- The effects are largely confined to the package.
- No fragments of appreciable size or range are to be expected.
- An external fire must not cause the simultaneous explosion of the total contents of a package of such items.
- Items may be classified as inert for storage purposes but may be subject to Part 173, Title 49 CFR, for transport (as reviewed on an individual basis).

The results obtained for LP 1845 and LP 1846 are presented in Figures 3 and 4, respectively. The current interim classification for these materials is DOT Class B (DOD Class/Division 1.3). Formal classification will be done when specification on package items for transportation are established and tests are conducted on the packages.

TB 700-2  
NAVSEAINST 8020.8  
TO 11A-1-47  
DLAR 8220.1

SUMMARY DATA SHEET

Date May 8, 1989

Sponsoring Agency U.S. Army AMCCOM

Contract No. DAAA21-88-D-0021

Explosive or Propellant Identity (Type No.)

Spec. LP 1845 Batch 1845-1 MSDS-054

Mfg. Date 5/12/86

Detonation Test<sup>1</sup>

		Detonated	Burned	Fragmented			
		Yes	No	Yes	No	Yes	No
No. 8 Blasting Cap	Test I	—	X	—	X	—	X
	Test II	—	X	—	X	—	X
	Test III	—	X	—	X	—	X
	Test IV	—	X	—	X	—	X
	Test V	—	X	—	X	—	X

Samples: Five 2-inch cubes.

Test: One blasting cap per sample.

Ignition and Unconfined Burning Test<sup>1</sup>

	Exploded	Average Burning Time	
	Yes	No	Seconds
One 2-inch cube	—	X	4-1/2 min
One 2-inch cube	—	X	4-1/2 min
Four 2-inch cubes	—	X	5-1/2 min

Samples: Six 2-inch cubes.

Thermal Stability<sup>1</sup>

Test: 48 hours at 75°C in vented oven

Reaction

None

Card Gap Test

50% value N/A (no. of cards)

Comment

No detonation with 0 cards

Impact Sensitivity Test

Bureau of Explosives Impact Apparatus

Ten 3-3/4" (±1/16") Drop Test			Ten 10" (±1/16") Drop Test		
10 Trails			10 Trails		
Number of Trails Exhibiting			Number of Trails Exhibiting		
Explosion	Decomposition	No Reaction	Explosion	Decomposition	No Reaction
Flame and	Smoke	No Smoke	Flame and	Smoke	No Smoke
Noise	No Noise	No Noise	Noise	No Noise	No Noise
<u>0</u>	<u>0</u>	<u>10</u>	<u>0</u>	<u>0</u>	<u>10</u>

APPROVED:

Test Director \_\_\_\_\_ Test Department Head \_\_\_\_\_

ASSIGNED CLASSIFICATION

DOT Forbidden  
DOT Restricted\*  
DOT Class A  
DOT Class B  
DOT Class C  
UN Number

DOD Approval (see Para 3-2)

Signature \_\_\_\_\_

Title \_\_\_\_\_

Organization \_\_\_\_\_

\* Shipping instructions are to be requested from DOT.

1. All tests conducted using a 2" diameter polyethylene bottle filled with 8 cubic inches of LGP.

Figure 3. Summary Data Sheet for LP 1845

TB 700-2  
NAVSEAINST 8020.8  
TO 11A-1-47  
DLAR 8220.1

# SUMMARY DATA SHEET

Date May 8, 1989

Sponsoring Agency U.S. Army AMCCOM

Contract No. DAAA21-88-D-0021

## Explosive or Propellant Identity (Type No.)

Spec. LP 1846 Batch 1846-03 MSDS-111

Mfg. Date 10/12/87

## Detonation Test<sup>1</sup>

No. 8 Blasting Cap

Test I  
Test II  
Test III  
Test IV  
Test V

### Detonated

Yes	No
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>

### Burned

Yes	No
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>

### Fragmented

Yes	No
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>

Samples: Five 2-inch cubes.

Test: One blasting cap per sample.

## Ignition and Unconfined Burning Test<sup>1</sup>

One 2-inch cube  
One 2-inch cube  
Four 2-inch cubes

### Exploded

Yes	No
—	<u>X</u>
—	<u>X</u>
—	<u>X</u>

### Average Burning Time

Seconds
<u>7 min</u>
<u>6 min</u>
<u>7 min</u>

Samples: Six 2-inch cubes.

## Thermal Stability<sup>1</sup>

Test: 48 hours at 75°C in vented oven

### Reaction

None

## Card Gap Test

50% value N/A (no. of cards)

### Comment

No detonation with 0 cards

## Impact Sensitivity Test

### Bureau of Explosives Impact Apparatus

Ten 3-3/4" (±1/16") Drop Test

10 Trails

Number of Trails Exhibiting

Explosion Flame and Noise	Decomposition Smoke No Noise	No Reaction No Smoke No Noise
<u>0</u>	<u>0</u>	<u>10</u>

Ten 10" (±1/16") Drop Test

10 Trails

Number of Trails Exhibiting

Explosion Flame and Noise	Decomposition Smoke No Noise	No Reaction No Smoke No Noise
<u>0</u>	<u>0</u>	<u>10</u>

## APPROVED:

Test Director \_\_\_\_\_ Test Department Head \_\_\_\_\_

### ASSIGNED CLASSIFICATION

DOT Forbidden
DOT Restricted*
DOT Class A
DOT Class B
DOT Class C
UN Number

### DOD Approval (see Para 3-2)

Signature \_\_\_\_\_

Title \_\_\_\_\_

Organization \_\_\_\_\_

\* Shipping instructions are to be requested from DOT.

1. All tests conducted using a 2" diameter polyethylene bottle filled with 8 cubic inches of LGP.

Figure 4. Summary Data Sheet for LP 1845



## VULNERABILITY TESTING OF LIQUID PROPELLANT LP 1846

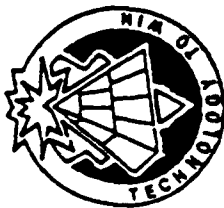
J.Q. Wojciechowski and C.S. Leveritt  
USA Ballistic Research Laboratory  
Aberdeen Proving Ground, MD 21005-5066

### ABSTRACT

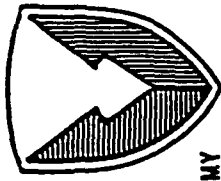
Liquid propellants consisting of hydroxylammonium nitrate (HAN), triethanolammonium nitrate (TEAN), and water are currently being investigated for use in large and medium caliber weapon systems. It is now required by the US Government that any new munition pass specified tests classifying it as an insensitive munition. Also, for weapons systems design, it is imperative that an analysis of the vulnerability of the propellant is available.

Precision shaped charges have been fired into 5 L of LP 1846 in a polyethylene container inside an armored personnel carrier. Certain test conditions were varied specifically conditioning armor. Analysis of pressure and temperature measurements within the vehicle showed little difference from firing the same charge through 5 L of water. Propellant remaining at the conclusion of the test reveals that the propellant did not burn. All tests were performed with hollow polyethylene balls in the container to break up the shock wave due to hydraulic ram. One test performed without the baffling showed a much greater reaction.

Current test results indicate that LP 1846 can pass two of the required insensitive munitions tests. Testing different size and dimensioned containers is planned to determine weapon system design guidelines and complete the required insensitive munitions tests.



BALLISTIC RESEARCH LABORATORY

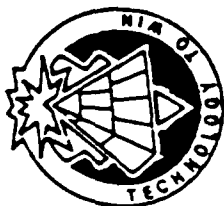


US ARMY  
LABORATORY COMMAND

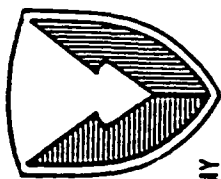
# Vulnerability Testing of Liquid Propellant LP 1846

*Josephine Q. Wojciechowski  
Charles S. Leveritt  
Walton T. Robinson*

USA Ballistic Research Laboratory  
Aberdeen Proving Ground, MD 21005-5066



# Vulnerability Test Plan Objectives

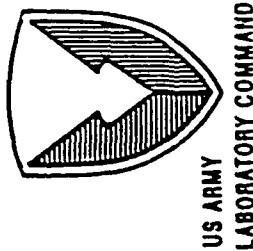


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- Conduct evaluation of candidate LGP to realistic battlefield threats
- Provide system designers with guidelines for container design
- Satisfy Insensitive Munitions requirements



## Insensitive Munitions Requirements



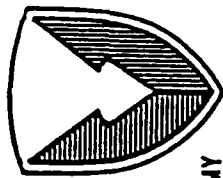
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TEST	CRITERIA
Fast Cook Off (FCO)	No reaction more severe than burning
Bullet Impact (BI)	No reaction more severe than burning
Sympathetic Detonation (SD)	Acceptor munitions will not detonate
Fragment Impact (FI)	No reaction more severe than burning
Slow Cook Off (SCO)	No reaction more severe than burning
Shaped Charge Jet (SCJ)	No detonation
Shaped Charge Spall (SCS)	No sustained burning



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## Section 1 Test Plan



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- Containers

- 1.5 gallon polyethylene (3.3 x 9.5 x 14.7)

- Conditioning

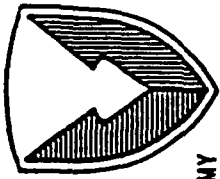
Jet	Spall
- 5" RHA	- 1" RHA
- 2" RHA	
- 0" RHA	

- Baffling

- Hollow Balls

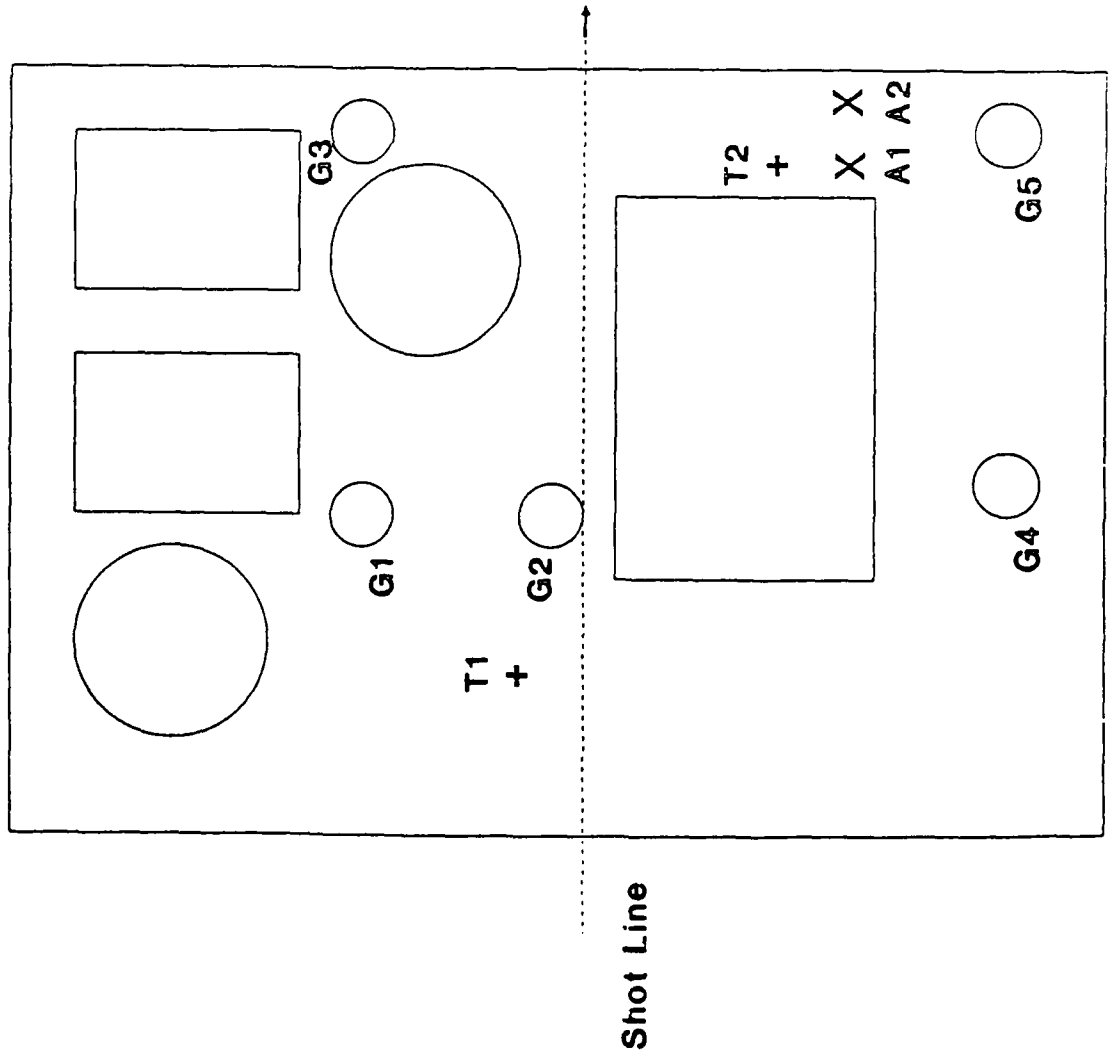


# Diagram of Test Instrumentation



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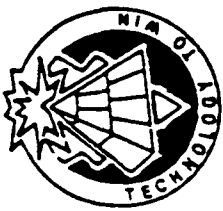
BALLISTIC RESEARCH LABORATORY



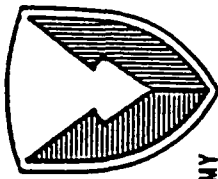
G1-G5 - Pressure Transducers  
(PCB Model 113A24)

T1-T2 - Thermocouples  
(.005"/Type K)

A1-A2 - Air Sample Ports

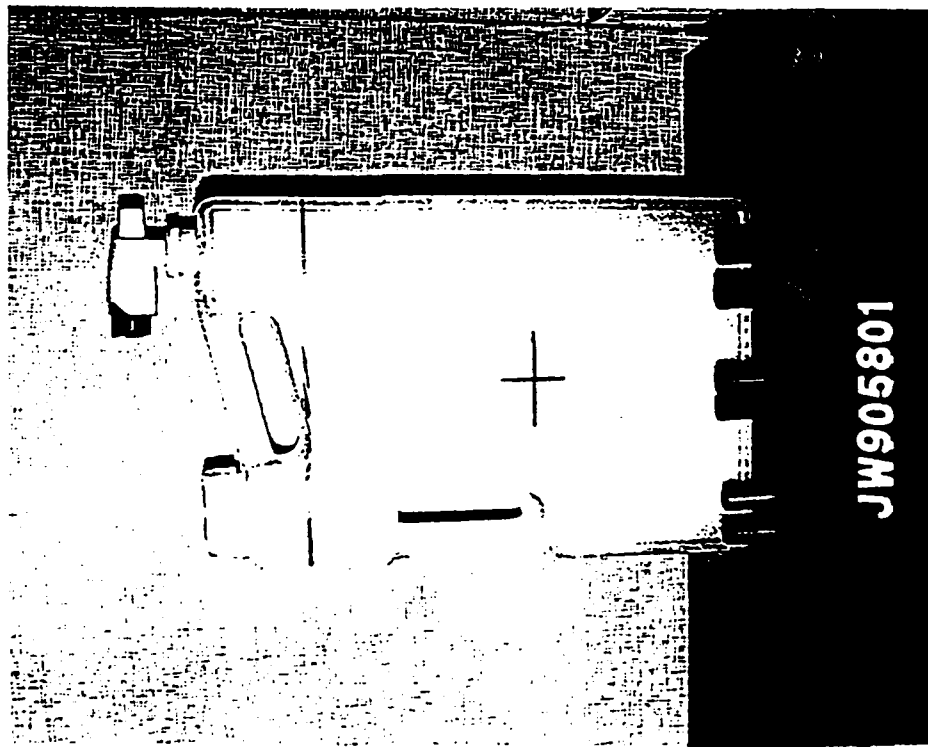


## Test Set-Up - Jet



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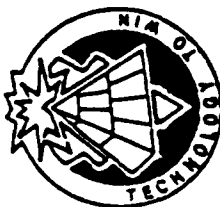
BALLISTIC RESEARCH LABORATORY



Container

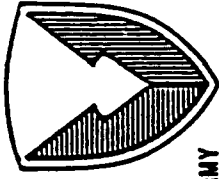


Witness Plate Arrangement

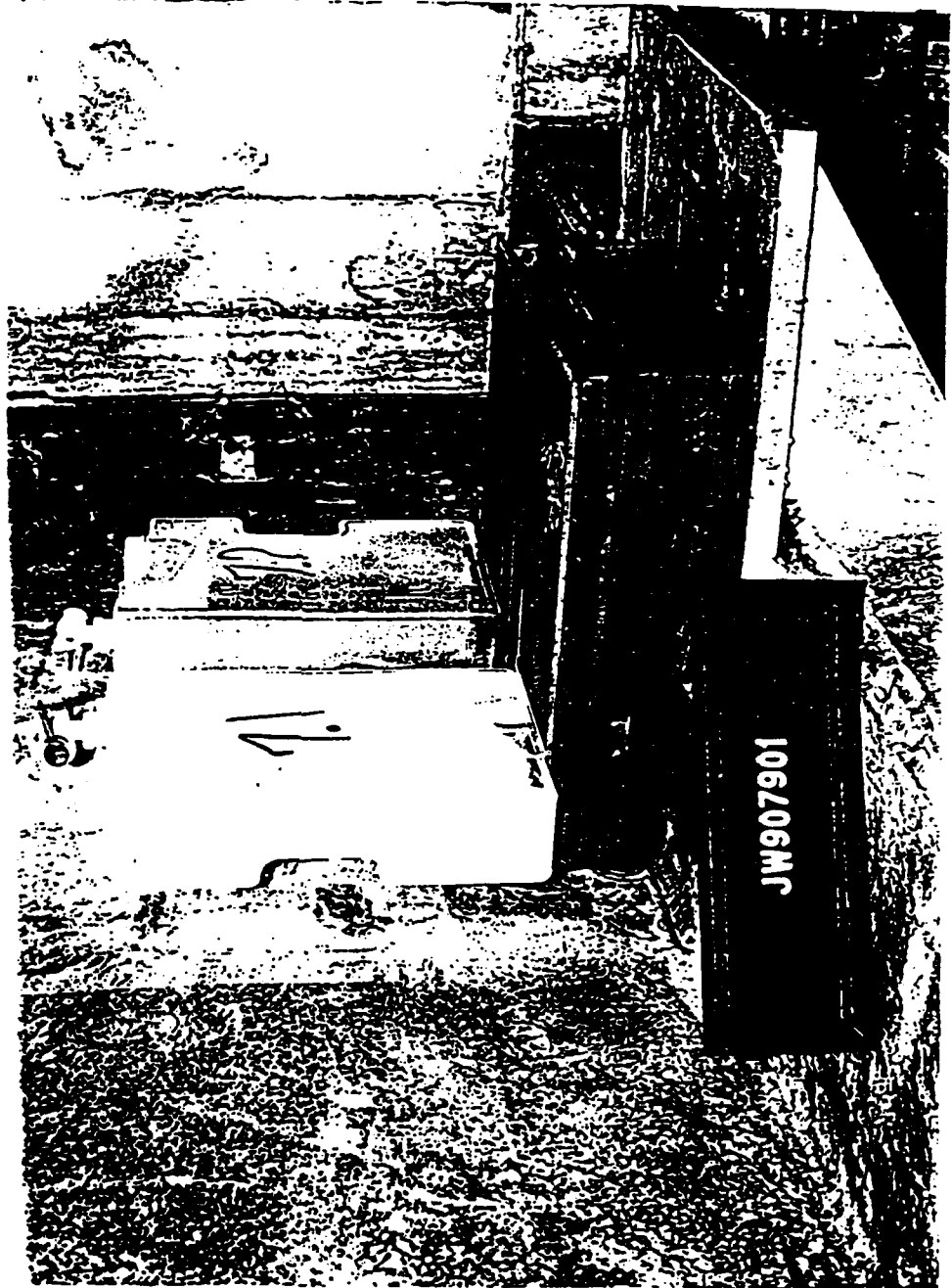


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## Test Set-Up - Spall

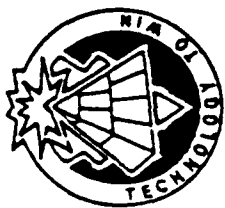


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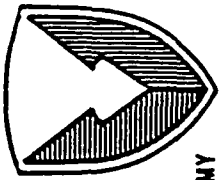
Container and Witness Plates





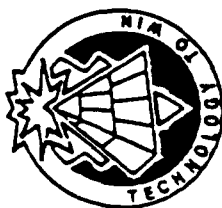
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## Test Conditions for Shots 1-9

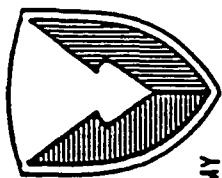


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Shot No.	Type	Material	Armor	Baffling
1	Jet	Water	5" RHA	No
2	Jet	LP	5" RHA	Yes
3	Jet	LP	2" RHA	Yes
4	Jet	LP	None	Yes
5	Jet	LP	2" RHA	No
6	Jet	LP	None	Yes
7	Spall	LP	1" RHA	No
8	Spall	LP	1" RHA	No
9	Jet	Water	None	No



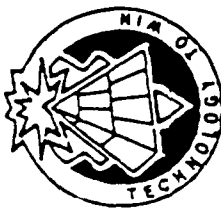
## Results of Vulnerability Test Shots 1-9



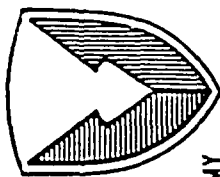
### BALLISTIC RESEARCH LABORATORY

Shot No.	Pressure Gages										Witness Plates			HAN/TEAN	
	G1		G2		G3		G4		G5		Top	Middle	Bottom	Before	After
	Pm	Imp	Pm	Imp	Pm	Imp	Pm	Imp	Pm	Imp					
1											0	0	0		
2			13	2							0	0	0	3.13	2.99
3			18	2							0	0	0	3.13	2.94
4	16	5	30	6	7	2	10	6	4	2	0.30	0	0	3.13	2.90
5	59	17	93	21	8	5	49	24	27	24	2.88	1.66	0.2	3.15	2.25
6	17	5	34	5	5	2	8	4	7	2	0.13	0	0	3.15	2.44
7	15	3									0	0	0	3.14	3.15
8	15	3	41	9							0	0	0	3.14	3.15
9	12	5	29	5							0	0	0		

\* Pm = Maximum Pressure (psi)  
Imp = Impulse (psi-ms)



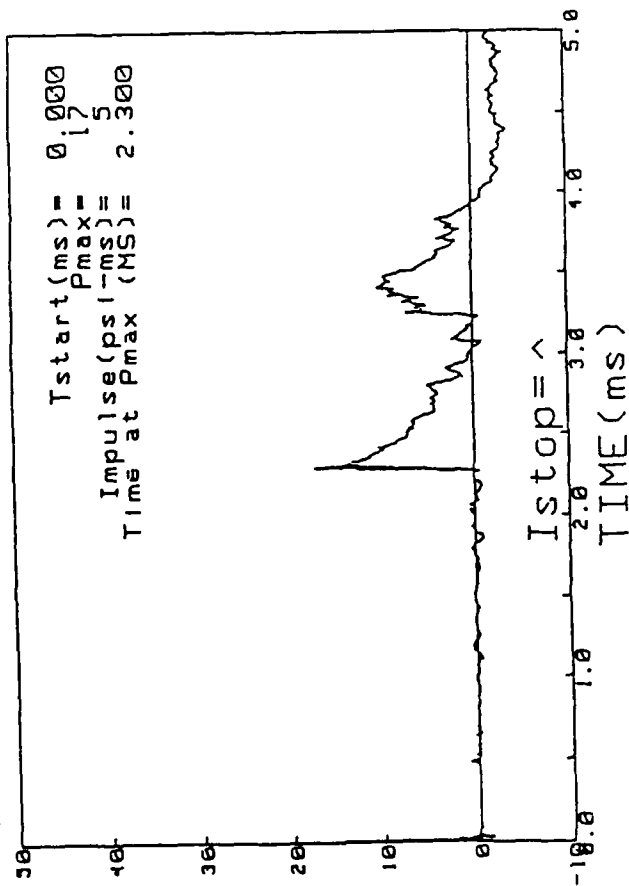
# Pressure Traces



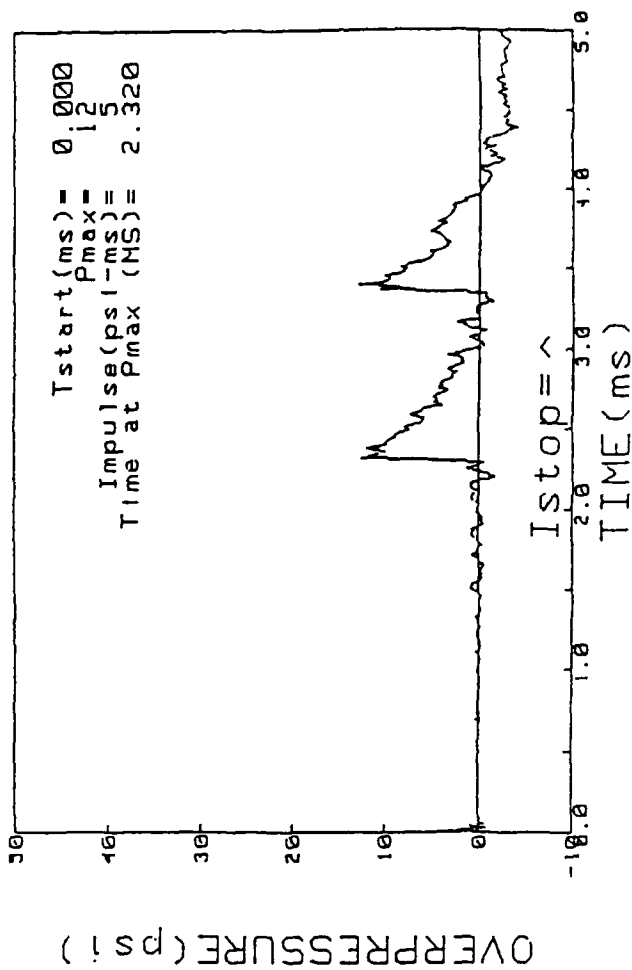
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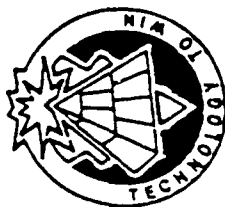
BALLISTIC RESEARCH LABORATORY

SHOT NO. 6/G1

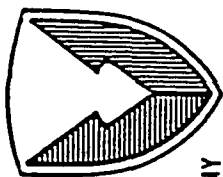


SHOT NO. 9/G1





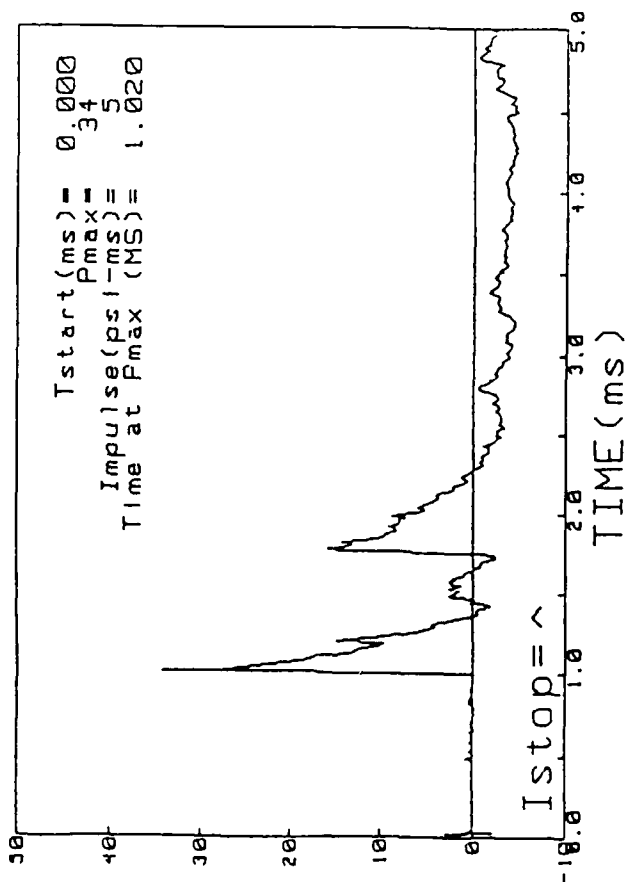
# Pressure Traces



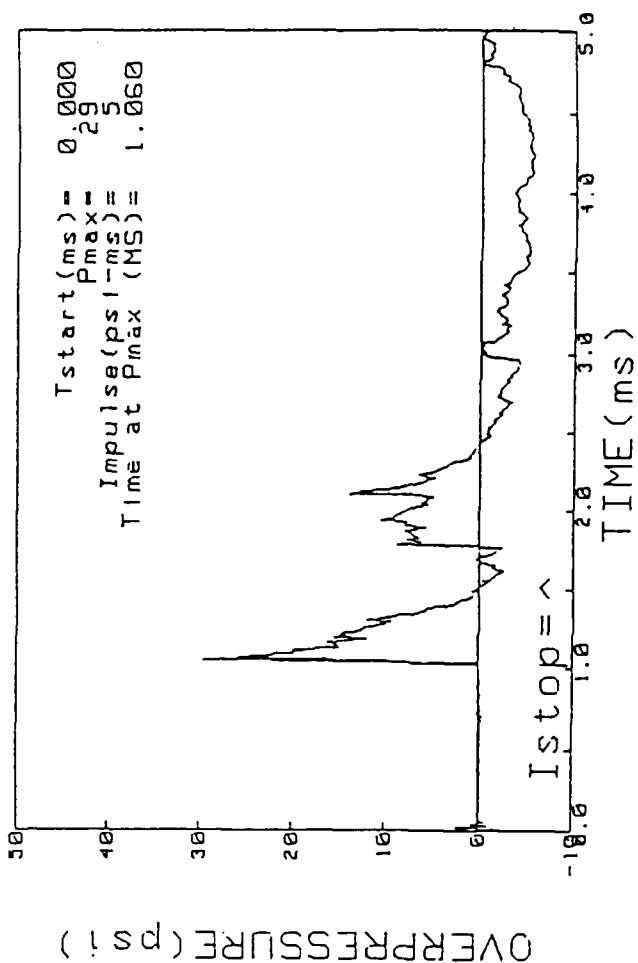
US ARMY  
LABORATORY COMMAND

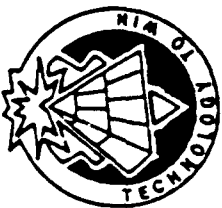
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SHOT NO. 6/G2



SHOT NO. 9/G2

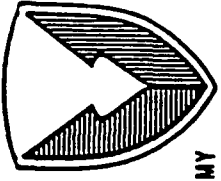




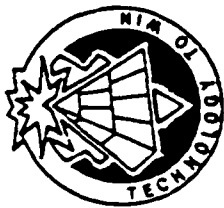
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## Conclusions

- Insensitive Munitions Shaped Charge Jet test requirement of "No Detonation" was achieved
- Insensitive Munitions Shaped Charge Spall test requirement of "No Sustained Burning" was achieved
- Reduction of hydraulic ram effects will be required for reduced vulnerability of liquid propellants

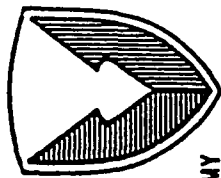


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LABORATORY COMMAND

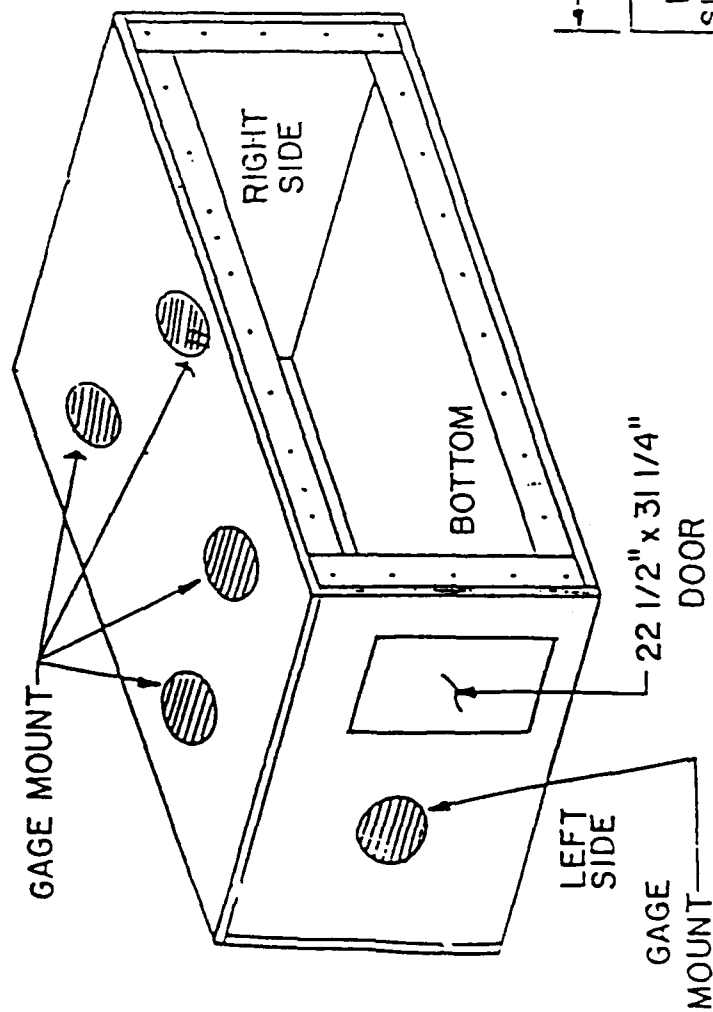


# New Test Fixture

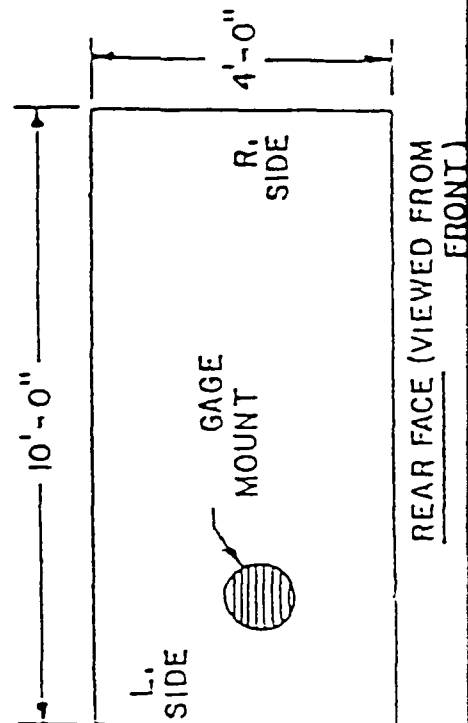
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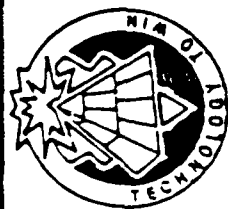
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LABORATORY COMMAND



NOTE:  
BOX INSIDE DIMEN.  
116" LONG  
70.14" WIDE  
44" HIGH



Two Inch Mild Steel Box



BALLISTIC RESEARCH LABORATORY

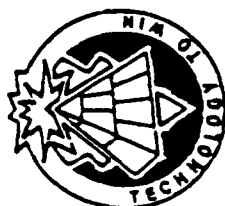
## Next Series of Tests

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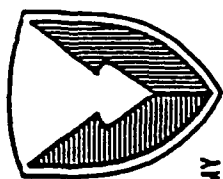
- Test conservatively, with baffles

### Containers

- Type 1 - 1.5 gal (3.3 x 9.5 x 14.7)
- Type 2 - 6 gal (4 x 18 x 18)
- Type 3 - 5 gal (6 x 8.5 x 13.5)
- Type 4 - 12 gal (4 x 24 x 30)
- Shot 1. Type 1 Cont., Water, No Armor
- Shot 2. Type 1 Cont., LGP, No Armor, Baffling
- Shot 3. Type 2 Cont., Water, HIP Armor
- Shot 4. Type 2 Cont., LGP, HIP Armor, Baffling
- Shot 5. Type 2 Cont., Reinforced, LGP, HIP Armor, Baffling
- Shot 6. Type 4 Cont., Water, HIP Armor
- Shot 7. Type 4 Cont., LGP, HIP Armor, Baffling
- Shot 8. Type 4 Cont., Reinforced, LGP, HIP Armor, Baffling
- Shot 9. Type 3 Cont., Water, HIP Armor
- Shot 10. Type 3 Cont., LGP, HIP Armor, Baffling



## Additional Testing Planned



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Phase 1 - Evaluate reactions of LP in a simulated bustle.

Phase 2 - Evaluate reactions of LP when stored under pressure.

Phase 3 - Evaluate the effect of initiating warheads stored adjacent to LP.

Phase 4 - Evaluate the ignitability of a ruptured LP feed line, 500 psi max.

Phase 5 - Evaluate the reaction of LP when spilled on a hot surface.

Phase 6 - Evaluate whether or not the LP will wick burn.

Phase 7 - Evaluate logistics containers.



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APPENDIX A

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5th Annual Conference on HAN-Based Liquid Propellant  
Structure and Properties

All sessions will be held in Bldg 330.

Charles S. Leveritt . . . . General Chairman

Sponsored by: LP Materials Team  
Advanced Ballistic Concepts Branch  
Interior Ballistics Division

Conference Room Phone	301-278-6842
	AV 298-6842
Information	301-278-6188
	AV 298-6188

Tuesday, Aug 22

0815 Registration and Coffee

0845 Welcome, Charles S. Leveritt, Deputy Program Manager,  
LP Program

0900 Arrangements, J. Wojciechowski, ABCB, BRL

Session I: Ronald A. Sasse', BRL, Presiding

0910 "The Effect of Pressure and Dissolved Gases on the Electrical Conductivity of Concentrated HAN Solutions and Liquid Propellants" by S. Murad and P. Ravi, University of Illinois at Chicago, Chicago, IL

0940 "Estimating Solution Densities for Mixtures Containing HAN" by D. W. Cawlfeld, Olin Chemicals, Charleston, TN

1010 "Investigation of FTIR Techniques for Determination of Ammonium Nitrate, Nitric Acid and Hydroxylamine in HAN-Based Liquid Propellants" by G. Singh (University of MD), R. A. Sasse' and R. A. Fifer, BRL, Aberdeen Proving Ground, MD

1030 Break

1050 "The Anomalous Behavior of HAN-Based Liquid Propellant During Analysis - Part 1 Isothermal Studies" by S. Westlake and P. Bunyan, RARDE, Waltham Abbey, UK

1110 "The Anomalous Behavior of HAN-Based Liquid Propellant During Analysis - Part 2 Adiabatic Studies" by P. Bunyan and S. Westlake, RARDE, Waltham Abbey, UK

1130 Lunch

Tuesday, Aug 22

Session II: Richard C. Thompson, University of MD, Presiding

- 1300 "Raman Spectroscopy of Liquid-Phase Reactions in HAN-Based LPs"  
by R. A. Beyer and M. W. Teague, BRL, Aberdeen Proving  
Ground, MD
- 1320 "Nonlinear Spectroscopy of Water Droplets Containing Nitrates"  
by R. K. Chang, A. Serpenguzel, and P. Chen, Yale  
University, New Haven, CT
- 1420 "Shock Tube Ignition of TEAN in Nitrous Oxide" by  
R. A. Beyer, BRL, Aberdeen Proving Ground, MD
- 1440 Break

Session III: Richard Biddle, Thiokol Corp., Presiding

- 1500 "The Effects of Hydrodynamics on HAN-Based Liquid Propellant  
Combustion" by S. R. Vosen, Sandia National Laboratories,  
Livermore, CA
- 1520 "Deducing Useful Data From Images of HAN-Based Liquid Propellant  
Combustion" by R. C. Armstrong and S. R. Vosen, Sandia  
National Laboratories, Livermore, CA
- 1540 "Liquid Propellant Injector/Combustor Design and Test Results"  
by R. Rychnovsky, Sandia National Laboratories,  
Livermore, CA
- 1600 "Analyses of the Liquid Propellant Injector/Combustor" by  
S. K. Griffiths, Sandia National Laboratories,  
Livermore, CA
- 1620 Close

Wednesday, Aug 23

0830 Coffee

Session III: Eli Freedman, Freedman Assoc., Presiding

0900 "Reaction Model and Mechanism for HAN-Based Liquid Propellants"  
by N. Klein, BRL, Aberdeen Proving Ground, MD

0930 "Suggested Specifications for HAN-Based Liquid Propellants"  
by R. Biddle, Morton-Thiokol, Elkton, MD

0950 "Development of Analytical Methodology for Liquid Propellants"  
by S. Griff, GEO-Centers, Hopatcong, NJ and W. D. Seals  
and E. Turngren, ARDEC, Dover, NJ

1010 "Determination of Excess Acid in Liquid Propellant" by R. A.  
Sasse'", BRL, Aberdeen Proving Ground, MD

1030 Break

Session V: Charles S. Leveritt, BRL, Presiding

1050 "Human Exposure and Occupational Health Surveillance of Liquid  
Gun Propellant (LGP) Workers" by MAJ D. L. Parmer and MAJ  
D. A. Smart, USABRDL, Fort Detrick, Fredrick, MD

1110 "An Overview of Chemical and Biological Processes Which May Lead  
to Degradation of HAN and TEAN in the Environment" by M. L.  
Taylor, M. A. Dosani, PEI Associates, Cincinnati, OH and C.  
Graham, USATHAMA, Aberdeen Proving Ground, MD

1130 Lunch

Wednesday, Aug 23

Session V: Continued

1300 "Hazard Classification Studies on HAN-Based Liquid Propellants"  
by W. Herrera, Southwest Research Institute,  
San Antonio, TX

1320 "Phase I - Vulnerability Studies on LGP 1846" by J. Q.  
Wojciechowski and C. S. Leveritt, BRL, Aberdeen Proving  
Ground, MD

1350 Open Discussion

1530 Close



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APPENDIX B

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Eli Freedman & Associates  
2411 Diana Road  
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Stanley Griff  
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Pittsfield, MA 01201-3698

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Sally Westlake  
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Jean Paul Picard  
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201-724-5378

Dawn Schorling  
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Aberdeen Proving Ground, MD 21005-5066

SLCBB-IB-B

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301-278-6110

James DeSpirito  
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Nathan Klein  
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John Knapton  
301-278-6170

Charles Leveritt  
301-278-6185

Cris Watson  
301-278-6103

SLCBB-IB-I

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Robert Fifer  
301-278-6806

Rose Pesce-Rodriguez  
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Research Triangle Park, NC 27709-2211

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Aberdeen Proving Ground, Edgewood Area 21005

Carolyn A. Graham  
301-671-2054



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